Description and Evolution of the Escondida Porphyry Copper Deposit, Antofagasta Region, Northern Chile

Ruben Agustin Padilla-Garza

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Description and Evolution of the Escondida Porphyry Copper Deposit, Antofagasta Region, Northern Chile

by

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2003

THE UNIVERSITY OF ARIZONA GRADUATE COLLEGE

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ABSTRACT

The Escondida porphyry copper deposit is one of several giant porphyry copper deposits that lie along a Late Eocene-Oligocene magmatic arc in the Atacama desert of northern Chile. Escondida is characterized by structurally-controlled overprinting of magmatic and hydrothermal events that occurred in three discrete pulses at 38, 36, and 34 Ma. The mineralized intrusive stock at Escondida, like other nearby copper deposits, are localized at the intersection of extensional zones formed along strike-slip faults of the regional Domeyko Fault System with regional NW lineaments. These structural intersections are also associated with large magnetic anomalies.

The propylitic, potassic, and quartz-sericitic hydrothermally altered mineral assemblages are centered on a 38 Ma granodioritic stock complex composed of at least three phases. Approximately two million years later (36 Ma), rhyolitic intrusive and extrusive rocks, and sulfide-rich veins of an advanced argillic hydrothermal event affected the granodioritic stock and the veins of the potassic and quatz-sericitic events. A Re/Os age of 33.7 ± 0.3 Ma on a molybdenite sample from a polymetallic vein that cuts the younger rhyolite defines a younger hydrothermal event close to 34 Ma. The magmatic activity ended with the emplacement of barren rhyodacite dikes close to 34 Ma. By the time all three hydrothermal events had formed, the hypogene copper grade of the deposit varied between 0.2 and 1% Cu, reflecting varying degrees of overprinting by successive Cu mineralization stages.

The temperatures of homogenization of primary fluid inclusions from quartzorthoclase (Stage A), quartz-sericite (Stage B), and quartz-alunite-bearing veins (Stage C) vary between 500 ° and 560 °C, 280 ° and 380 °C, and 200 ° and 340 °C, respectively, with estimated depths of trapping ranging from 3.0 to 1.5 km.

The δ^{34} S values of sulfide minerals of the potassic event range from -3.2 to -2.0, whereas values from the quartz-sericitic event vary between -1.1 and +0.6 per mil. This suggests a common source of magmatic sulfur, but indicates that sulfides of Stage B were not formed by leaching sulfides from Stage A. The δ^{34} S values of Stage C are within a large range that varies between -2.5 and +2.7 per mil, which suggests that sulfides from the advanced argillic event may have formed, in part, by leaching sulfides for water coexisting with igneous and hydrothermal minerals indicate a main magmatic component associated with the evolution of hydrothermal stages A and B and the mixing with meteoric water at the lower temperatures of Stage B and during the development of the advanced argillic event.

The Sm/Nd and Rb/Sr isotopic values of the Paleocene-Oligocene igneous rocks from the Escondida district, like other porphyry copper districts of northern Chile, vary between 0 and 2 $\epsilon_{Nd(time)}$ and have ${}^{87}Sr/{}^{86}Sr_i$ ratios close 0.705. The ${}^{187}Os/{}^{188}Os$ ratios of two magnetite samples from the Escondida stock yielded 1.70 and 0.28, and a value of 0.67 was reported from a sample of hydrothermal magnetite. These data suggest that the sources of metals and magmas have a large (>75 vol. %) radiogenic component either from the mantle or from lower crust of short residence before melting to generate the magmas that formed the Escondida stock. The Late Eocene-Oligocene igneous rocks from Escondida have steep REE patterns that may have formed by low partial melting in a garnet-stable zone. However, the connection with a high copper budget is not clear since there is no partitioning coefficient information for copper. Other ways to explain the steep REE patterns are: a) contamination of LREE and probably metals from subducted sediments or b) anomalous composition of the lithospheric mantle along the axis of the large porphyry copper belt of northern Chile.

At the Escondida porphyry copper deposit, magmas generated either in the mantle or in radiogenic lower crust intruded into continental crust that was more than 57 km thick at the end of a magmatic event that lasted 12 Ma. The overprinting of three separate magmatic and hydrothermal pulses during a period of approximately 6 Ma resulted in high hypogene copper grade. After the formation of the hypogene system, the arid climate and tectonic quiescence of the region favored the formation and preservation of one the world's largest and richest known supergene enrichment blankets.

INTRODUCTION

This dissertation presents an update of the geology of the Escondida porphyry copper deposit in northern Chile (Fig. 1), which currently is one of the two largest copper producers in the world. In 1999 it was producing more than 800,000 tons of fine copper per year (http://www.bhpbilliton.com). Its reserves and contiguous resources in 1999 were 2,262 million tons with 1.2 weight percent of copper (http://www.bhpbilliton.com). The deposit was discovered in 1981 and began production in 1989. The geology and history of its discovery and development have been outlined by Ortiz et al. (1996) and summarized by Padilla et al. (2001).

The deposit is one of several giants in northern Chile, in and along the Domeyko Cordillera and the western limit of the Preandean Basin provinces, including Chuquicamata, El Salvador, El Abra, and Collahuasi (Fig. 1). This line of great ore deposits lies 100 km west of the high Andes. Escondida is similar in many respects to these other ore systems, being associated with calc-alkaline porphyry intrusions that have invaded a volcanic pile. The basement is characteristic of this setting consisting of lower Paleozoic sedimentary rocks overlain by late Paleozoic-Early Triassic-age rhyolitic rocks, which in turn are overlain by a varied succession of Mesozoic clastic rocks with a few volcanic strata. Early Tertiary volcanic rocks, dominantly andesite, overlie the older successions and host the porphyry intrusions at Escondida.

Information from drill holes and surface exposures was used to develop the first geological description and geochronology of alteration of the deposit (Alpers, 1986; Ojeda, 1986, 1990; Alpers and Brimhall, 1988, 1989). Since the publication of those works, additional drill holes and mining have further exposed the ore body. In 2000 and

2001 Richards et al. published two papers emphasizing the geochronology and geochemistry of igneous rocks at the district scale.

This dissertation seeks to present the evolution in time and space of the magmatic-hydrothermal system of the Escondida deposit, as well as its sources of fluids, metals, and magmas, in a comprehensive fashion. It includes: (1) a study of the paragenesis, zoning, and geochemistry of the different magmatic-hydrothermal event, (2) time control of the magmatic and mineralizing events, (3) a review of the structural geology at deposit scale, and (4) review of the regional tectonic setting and district geology.

The review of regional and district geology includes compilation of public data, mapping at district scale, and mapping along two regional east-west geological transects. The structural interpretation is based on mapping of the Escondida open pit. The study of the magmatic-hydrothermal evolution includes the separation of intrusive and hydrothermal events and their petrographic and mineragraphic characterizations. Sources of magmas were researched using Sm-Nd and trace element geochemistry. Sources of fluids and sulfur were investigated using stable isotopes and fluid inclusion data from the different hydrothermal phases, while sources of metals were studied by ¹⁸⁷Os/¹⁸⁸Os ratios. Fluid inclusions and stable isotope data were also used to explore fluid history and the physicochemical conditions during the precipitation of each mineralizing event.

The chronological evolution of the different magmatic and hydrothermal events was determined using U-Pb, 40 Ar/ 39 Ar, and Re-Os geochronology of appropriate mineral and rock phases. For example, U-Pb dated the different magmatic pulses, 40 Ar/ 39 Ar also dated intrusive rocks in addition to hydrothermal events, and Re-Os was used to date

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molybdenite. Thus, this comprehensive approach yielded a most complete picture of the temporal evolution of the Escondida porphyry copper deposit.



Fig. 1: Location of the Antofagasta region, the Domeyko Fault System and associated porphyry copper districts, the Escondida Segment, and the Escondida district (after Mpodozis et al., 1993). Age of Escondida from Richards et al. (1999) and this study. For section A-A'see Figure 2.

CHAPTER 1

REGIONAL GEOLOGY

Five north-south morphotectonic-physiographic provinces characterize northern Chile (Sillitoe and McKee, 1996). From the Pacific coast eastward they are: Coastal Range, Central Depression, Cordillera de Domeyko, Preandean Basin, and Andean Cordillera (Fig. 2). Escondida is located at the eastern limit of the Cordillera de Domeyko province (Fig. 2). The Cordillera de Domeyko province is approximately 50 km wide, and is formed by north-south elongated ranges and shallow gravel-filled basins. Elevations vary from 2,000 to 4,500 m above sea level.

The earliest stage of geological evolution in this section of northern Chile is the evolution of the western margin of Gondwana during the Paleozoic (Ramos, 1989). In the Preandean Basin, late Precambrian to middle Paleozoic turbidites and volcano-sedimentary sequences accumulated and were deformed when intra-arc basins opened and closed between Precambrian fragments. These fragments were located in front of the continent and were accreted during the middle Paleozoic (Ramos, 1989; Fig. 2). This early stage was followed by uplift and the development of a middle Paleozoic magmatic arc in the present position of the Cordillera de Domeyko and the Preandean Basin provinces (Mpodozis and Ramos, 1990; Fig. 2). A passive margin formed from the middle Silurian to the late Carboniferous, with rifting of the western margin of the continent (Bahlgurg and Hervé, 1997). During this time a second succession of turbidites accumulated along fluvial channels in the uplifted continental basement (Cordillera de

Domeyko and Preandean Basin) and in deep extensional oceanic basins formed in the Coastal Range and in the Central Depression Provinces (Bahlgurg and Hervé, 1997; Fig. 2). During the Permian to the early Triassic, rhyolitic rocks were emplaced in the western margin of the continent (Mpodozis and Ramos, 1990). By the end of the Paleozoic, the western margin of this part of the Paleozoic continent and its oceanic edge were already formed, with a thick continental crust lying on the east and turbidite basins, probably deposited on oceanic crust, lying to the west. Today, the Cordillera de Domeyko is located at the boundary between these two zones (Fig. 2).

The Mesozoic time was characterized by the development of a magmatic arc in the Coastal province and an extensional back-arc basin over the Paleozoic basement of the Central Depression and on the Cordillera de Domeyko provinces (Sillitoe, 1981, 1988; Mpodozis and Ramos, 1990; Fig. 2). The last stage in the formation of this region involved the development of a continental margin where three Andean-type magmatic arcs evolved from the late Cretaceous through the late Cenozoic periods. These formed along the eastern limit of the Central Depression, the Cordillera de Domeyko, and the Andean Cordillera provinces (Sillitoe, 1981, 1988; Mpodozis and Ramos, 1990; Fig. 2). The largest porphyry copper systems of the region formed within the Precordillera de Domeyko and its western margin between 42 and 31 Ma (Gustafson and Hunt, 1975; Sillitoe, 1988; Zentilli et al., 1994; Cornejo and Mpodozis, 1996; Richards et al., 2000). From 31 Ma to the present, climatic changes favored the formation and preservation of enrichment blankets over the porphyry copper deposits (Alpers and Brimhall, 1988; Sillitoe and McKee, 1996).



Fig. 2: West to east section (A-A'), looking north, from Antofagasta to Escondida and a generalized tectonostratigraphic column. Section A-A' includes the main morphotectonic provinces and the main fault systems of the region. Compilations after Boric et al. (1990); Mpodozis and Ramos (1990); Mpodozis et al. (1993); Coney and Evenchick (1994); and Prinz et al. (1994).

Regional Structure

During the Mesozoic, an extensional back-arc basin was situated in the region of the Cordillera de Domeyko and the Central Depression. The distribution of Paleozoic and Mesozoic rocks and the change of sedimentary facies of the rocks of the Mesozoic back-arc basin (Boric et al., 1990; Prinz et al., 1994; and Ardill et al., 1998) suggest that the eastern limit of the Mesozoic extensional back-arc basin developed roughly in the transition between the Paleozoic continental crust and Paleozoic oceanic turbidites. Therefore, during the Mesozoic, the eastern edge of the back-arc basin was probably delimited by syn-sedimentary normal faults (Fig. 2). This type of growth fault has been reported in the area of Quebrada Blanca by Tomlinson and Blanco (1997a and b).

During the Late Cretaceous in the Cordillera de Domeyko, the normal faults of this Mesozoic basin were probably inverted with the consequent formation of thrust faults, north-south folds, and crustal thickening. Reutter et al. (1991) interpreted a minimum of 25 percent of shortening for this period. From the Eocene to the Miocene, the structural deformation in the Cordillera de Domeyko province was characterized by transcurrent tectonics with changing sense of movements (Mpodozis and Ramos, 1990; Reutter et al., 1991; Cornejo et al., 1996; Tomlinson and Blanco, 1997a and b).

The Domeyko Fault System is the main structural feature of the Cordillera de Domeyko province. Mpodozis et al. (1993) separated the Domeyko Fault System into five segments along its strike (Fig. 1). The Escondida district is located in the Escondida segment, which is characterized by cymoid-geometry (McKinstry, 1948) expressed as north-south elongated basins in a zone 200 km long by 20 to 50 km wide (Fig. 1). During the early Eocene, the faults of the Domeyko Fault System were active as transpressive structures, as is indicated by the first reverse strike-slip movements along the major faults (Cornejo et al., 1996, Tomlinson and Blanco, 1997b). This transpressional tectonism continued until 30 Ma in the southern part of the region near El Salvador (Cornejo et al., 1996). Near Escondida and in the Chuquicamata district, the faults of the Domeyko Fault System have moved as strike-slip structures over the past 40 Ma (Mpodozis et al., 1993; Tomlinson and Blanco, 1997a and b; Fig. 1). The only fault of the Domeyko system with reported significant lateral displacement is the West Fissure in Chiquicamata, where it truncates the copper deposit with a proposed left lateral movement of 35 km (Baker and Guilbert, 1987; Tomlinson and Blanco, 1997a and b; Dilles et al., 1997).

Paleomagnetic reconstruction of plate movements from the Late Mesozoic to the present indicates two main directions of subduction (Pardo Casas and Molnar, 1987; Scheuber and Reutter, 1992): a northwest-southeast direction older than 90 Ma; and a northeast-southwest direction younger than 70 Ma, with a transitional period between 90 and 70 Ma.

The Cretaceous sinistral sense of movement of the Atacama Fault System, on the western coast of northern Chile, accords with the northwest-southeast direction of convergence during the older period (Gonzales, 1996). The late Cretaceous compressional event that formed the thrust faults and north-south folds in the Cordillera de Domeyko probably corresponds with the 90 to 70 Ma period of rotation of stress direction, from northwest-southeast to northeast-southwest. Kinematic indicators of the Domeyko Fault System reported by different authors (Mpodozis et al., 1993; Boric et al., 1990; Tomlinson and Blanco, 1997b; Veliz and Padilla, 1997) indicate that the main

regional stress during the Paleocene-Miocene time changed its orientation at different times. The periods of sinistral sense of movement during the Cenozoic along the Domeyko system are in contradiction with the northeast-southwest direction of the main compressive stress, suggested by the direction of subduction during this period. Despite the northeast-southwest direction of subduction from 70 Ma to the present, the faults of the Domeyko Fault System have sporadically moved in a left-lateral sense, with a calculated northwest-southeast orientation of the principal stress. This is an important problem in the evolution of the Domeyko Fault System that has been addressed by Mpodozis et al. (1993) and by Tomlinson and Blanco (1997a); however, a detailed discussion of this problem is beyond the scope of this review.

Two of the largest porphyry copper districts of northern Chile are emplaced along faults of the Domeyko Fault System. North-northeast-striking faults have been associated with the emplacement of the porphyry copper system in Chuquicamata (Lindsay et al., 1995; Tomlinson and Blanco, 1997a), and a group of steeply dipping northwest-striking left-lateral faults are associated with the emplacement of the productive intrusive rocks at the Escondida district.

In northern Chile, the major structures of the Domeyko Fault System are observable in Landsat images. In addition to the known fault systems, two groups of major lineaments are also observed in Landsat images with orientations of N60^oW and N60^oE (Salfity, 1985). The geological significance of these lineaments is not clear, but most of the large, known porphyry systems of northern Chile are located at the intersection of these major lineaments with the Domeyko Fault System, including the Escondida district.



Fig. 3: Schematic section, looking north, from Antofagasta to Escondida showing the interpreted geological evolution of the region from the Late Paleozoic to the Cenozoic.

Summary and Interpretation of the Regional Geologic Setting

During the Late Precambrian and the Paleozoic, this part of northern Chile evolved as a part of the western margin of Gondwana (Ramos, 1989; Figs. 2 and 3), with a thick continental crust to the east and turbidite sediments towards the west, probably deposited on older oceanic crust. Today, the Cordillera de Domeyko is located at the boundary between these two zones (Fig. 2).

The Mesozoic marked an important change in the tectonic regime of the region. A new subduction zone was activated to the west, forming a magmatic arc in the present position of the Coastal Range province. Its extensional back-arc basin developed over the area occupied today by the Central Depression and the Cordillera de Domeyko provinces (Mpodozis and Ramos, 1990; Figs. 2 and 3). During the late Cretaceous and the entire Cenozoic, three Andean magmatic-arc types were developed, cutting and covering previous rocks (Figs. 2 and 3). The mineralization at Escondida and many of the largest porphyry copper districts of northern Chile are spatially and temporarily associated with the Eocene-Oligocene magmatic event (Sillitoe, 1988; Cornejo and Mpodozis, 1996; Richards et al., 2000; and this study).

The Cenozoic strike-slip structural deformation style of the Domeyko Fault System followed periods of structural extension and shortening (Boric et al., 1990; Mpodozis and Ramos, 1990; Reutter et al., 1991; Cornejo and Mpodozis, 1996; Prinz and Hillerbrandt, 1994; Tomlinson and Blanco, 1997; Ardill et al., 1998). In this study it is interpreted that the proto-Domeyko Fault System could have developed during the formation of the Mesozoic extensional back-arc basin as growth faults that marked the eastern edge of the extensional back-arc basin. It seems that this was not a continuous



Fig. 4. Geological map of the Escondida region. Located along the Domeyko Fault System, limited by the Sierra de Varas and the Zaldivar faults. Modified from Marinovic et al. (1992). Ages from Marinovic et al. (1992), Richards et al. (2000), and this study. NW major lineaments from LANDSAT image and magnetic high from Behn et al. (2000) and BHPB internal report.

structure but, more likely, was formed by a series of north-south faults that broke the western margin of the Paleozoic continent in a 10- to 50-km-wide strip. Perhaps fragments of the Paleozoic continental crust were dropped down toward the west, to form the basement of the eastern edge of the Mesozoic back-arc basin (Fig. 3). It is possible that from the Late Cretaceous to the early Cenozoic, the set of Mesozoic-aged faults were reactivated as thrust and transpressive faults that later moved as strike-slip structures, forming the present geometry of the Domeyko Fault System. It is suggested that the emplacement of productive magmas in the upper crust was favored by extensional zones along the strike-slip faults of the Domeyko Fault System. From 31 Ma to the present, the region of the Cordillera de Domeyko has been tectonically quiet, with low rates of denudation and climatic changes that favored the formation and preservation of enrichment blankets over the porphyry copper systems (Alpers and Brimhall, 1988; Sillitoe and McKee, 1996).

CHAPTER 2

DISTRICT GEOLOGY

The Escondida district comprises six copper deposits: Escondida Norte, Zaldivar, Pinta Verde, Carmen, Ricardo, and Escondida (Figs. 4 and 5). The Escondida deposit is the largest deposit located within the Escondida district. North-south-striking left-lateral strike-slip faults enclose a cymoidal shape that delimits the mineralized area in the district (Fig. 4).

East of the central fault (the Zaldivar fault; Fig. 4), Paleozoic intrusive, volcanic, and sedimentary rocks correlated with the Argomedo and La Tabla formations are exposed (Perelló, 1984; Marinovic et al., 1992; Richards et al.,2001, this study). The base of this succession includes andesite with subordinate sedimentary lenses cut by tonalite, granodiorite, and granite intrusions. These units are cut by and covered by Late Paleozoic rhyolite (Fig. 4). The Paleozoic andesite is fine-grained with trachytic texture and is regionally affected by low-grade metamorphism, characterized by epidotechlorite \pm tremolite; with up to 2 volume percent magnetite. The magnetism is a regional characteristic that differentiates Paleozoic andesite from Tertiary andesite, which is not magnetic. Whole-rock K-Ar analysis of the Paleozoic andesite in the Escondida district yielded apparent Jurassic ages of 196 \pm 14 Ma and 169 \pm 12 Ma (Perelló, 1984; Marinovic et al., 1992; Fig. 19). However, the trachytic andesite is clearly cut by a Late Paleozoic rhyolite (268 \pm 11, Marinovic et al., 1992; 265.8 \pm 2.1 Ma, Richards et al., 2000) at the Escondida Norte deposit. Therefore, the whole-rock, K-Ar Jurassic ages of the andesite probably indicate the age of metamorphism.

West of the Zaldivar fault (Figs. 4 and 5), Paleozoic rocks are overlain by marine and continental Mesozoic sedimentary rocks of the Profeta and Santa Ana Formations, respectively (Marinovic et al., 1992). The contact between the Paleozoic and Mesozoic units, exposed along the Antofagasta-Escondida highway, is an unconformity marked by conglomerate and sandstone that changes upward to shale, limestone, and calcareous limestone of the El Profeta Formation. The contact between the Triassic-Jurassic marine strata and overlying middle Cretaceous continental-subaqueous rock is gradational. These middle Cretaceous rocks of the Santa Ana Formation consist principally of calcareous sandstone, red sandstone, conglomerate, and shale interbedded with thin layers of red volcanic tuffs. The Mesozoic sedimentary succession is, in turn, overlain unconformably by late Cretaceous-Paleocene andesite, which correlates with the Augusta Victoria Formation (Perelló, 1984; Fig. 4).

The Paleozoic-Mesozoic-Paleocene section is cut by Eocene-Oligocene intrusions ranging from quartz diorite to granodiorite (Richards et al., 2000; Fig. 5). Oligocene-Miocene rhyolitic subvolcanic intrusive and extrusive rocks cut and cover the Escondida porphyry (Alpers and Brimhall, 1988). The specific time relationships between the different intrusive rocks and the hydrothermal evolution in the district have been described by Richards et al. (2000), and a detailed geochronological evolution of the Escondida deposit is presented in this study (see Table 5, Figs. 19, 20, and 28, and Chapter 4). The mineralization at Escondida, Zaldivar, and Escondida Norte is spatially and probably temporally related to the Eocene-Oligocene granodioritic stocks. In all three, alteration evolved from early potassic (that may have been synchronous with propylitic alteration) to sericite-chlorite, and quartz-sericite. These deposits also include the overprinting of a younger advanced argillic alteration event. At Escondida and Zaldivar, the intrusive rocks are hosted by Paleocene andesite, whereas at Escondida Norte they are hosted by rocks of the Paleozoic succession (Fig. 5). At Pinta Verde, Cu-Fe sulfides and copper oxides are hosted by biotite-altered Paleocene andesite, but no porphyry phases have been found in direct association with this deposit. Carmen is covered by gravel, and there is not enough drilling information to describe its main characteristics. The Ricardo deposit consists of secondary chalcocite rimming pyrite hosted by an Oligocene rhyolite (Fig. 5).



Fig. 5: **Simplified geological map of the Escondida district.** The left sense of movement of the Zaldivar fault is inconsistent with the apparent transtensional structural control, probably indicating earlier dextral sense of movement (see discussion in the text). Compilation from outcrop mapping and drill hole information. After Perelló (1984); Marinovic et al. (1992); and this study. Map in UTM coordinates.
CHAPTER 3

GEOLOGY OF THE ESCONDIDA DEPOSIT

Lithology

The Escondida porphyry copper deposit is associated with a 38 Ma granodiorite porphyry stock (see Chapter 4) hosted by andesite correlative with the Paleocene Augusta Victoria Formation (Perelló, 1984; Marinovic et al., 1992). Its shape is elliptical, elongated N30°-40°W, with a 4.5 km maximum axis and a 2.5 km minimum axis (Fig. 6). This granodiorite stock, known as the Escondida stock, is composed of at least four phases (Perelló, 1983; Quiroz, 1997).

The earliest two intrusive phases are porphyritic rocks that are similar in mineralogy but distinguished on the basis of their average content of phenocrysts, vein continuity, and intensity of alteration (Perelló, 1983; Quiroz, 1998). They are known as the Colorado Grande intrusion and the Escondida intrusion, respectively (Quiroz, 1998).

The Colorado Grande intrusion is a crowded porphyry with an average phenocryst content of 60 volume percent, whereas the phenocryst content of the Escondida intrusion averages less than 40 volume percent. In both intrusions the feldspar phenocryst size ranges between 1 and 5 mm, and rarely up to 8 mm. The phenocrysts are quartz, orthoclase, plagioclase, and biotite. Quartz phenocrysts (2-8 vol. %) have subrounded shape, with sizes between 0.5 and 3.0 mm, in some cases with undulose extinction. Plagioclase phenocrysts (60-70 vol. %), of oligoclase to andesine composition, have lengths between 0.5 and 5 mm and are euhedral to subhedral and show concentric compositional zoning. Orthoclase phenocrysts (20-30 vol. %) are between 0.5 and 3.0 mm in length, sub-euhedral, and show Carlsbad twining. Brown biotite books (1-3 vol.%) are euhedral, with diameters between 0.5 and 1.5 mm. The groundmass is composed of plagioclase, orthoclase, quartz, and biotite crystals smaller than 0.5 mm.

The third intrusive phase of the Escondida stock is the porphyry-breccia, which has a N10°W elongated shape, with a maximum axis of 1 km and a minimum axis of 250 m (Fig. 7). This third intrusive phase is similar in composition and in phenocryst content to the Escondida intrusive phase but includes mineralized fragments of the two earlier intrusive phases and the andesite. The average fragment content in this intrusive rock is approximately 8 volume percent; however, locally fragments increase to 60 volume percent, showing the texture of an intrusion breccia. Mineralized veins also crosscut the porphyry-breccia intrusive phase. Quiroz (1998) recognized narrow granodioritic dikes with quartz-sericite alteration and hypogene Cu-Fe sulfides that cut all previous intrusive phases.

Two rhyodacite intrusions with different textures and intensities of alteration intruded the Escondida stock after the development of the potassic and quartz-sericitic hydrothermal stages but before the development of the advanced argillic hydrothermal stage. These rhyodacitic bodies are informally called rhyolite dome and southwest hill rhyolite (Fig. 7). The first rhyodacitic intrusion was the rhyolitic dome with porphyritic texture that intruded the Escondida stock in the center of the deposit (Fig.7), probably closely after the intrusion of the porphyry system at 38 Ma (Fig. 28). This rock contains



Fig. 6: Lithology and main fault zones of the Escondida deposit, plan view at 2,800 m.a.s.l. List of symbols shown in figures 5 and 7. Compilation from drill hole information and mapping of the open pit. Approximate boundary of the Escondida open pit (1997) is shown. Map in local mine coordinates.



Fig. 7: Lithology of the Escondida pit. Ages of the Escondida stock and rhyolite from Zentilli et al. (1994), Richards et al. (1999), and this study. After Padilla et al. (2001).

angular and rounded embayed quartz phenocrysts less than 2 mm in diameter surrounded by a microcrystaline groundmass composed of quartz, feldspar, plagioclase, and biotite. The rhyolitic dome is always strongly silicified and argillized. The second rhyolite intruded as dikes between 36 and 34 Ma (Fig. 28). This dike has a phenocryst content of 60 volume percent. The sizes of phenocrysts range between 1 and 10 mm and are composed mainly of quartz, orthoclase, plagioclase, and biotite. The texture is tuffaceous, banded, and welded, with xenoliths of other rocks. This rock is normally weakly argillized and silicified, with strong alteration restricted to its contact with the host rock and along fault zones (Fig. 11).

The last intrusive event consists of unmineralized, weakly sericitized, narrow quartz monzonite dikes that cut the rhyolite (Fig. 7). A U-Pb age reported in this study (Fig. 23) indicates a crystallization age close to 34 Ma.

In the evolution of the Escondida porphyry system, at least three types of breccias were formed: intrusion breccias, cooling breccias, and pebble dikes. Intrusion breccias (fragments supported by igneous matrix) are associated with the third intrusive phase of the Escondida stock. Cooling breccias formed at the contact of the rhyolitic domes and the andesite. Mineralized and barren pebble dikes postdate the emplacement of the rhyolites and tectonic breccias of different ages (Fig. 7).

Faults

More than 1,800 faults and fractures in the Escondida pit were measured, included azimuth and dip, crosscutting relationships, and timing with respect to mineralization. These data were used to define the fault geometry presented in Figure 8. Of these structural data, 266 measurements include the trend and plunge of slickenlines observed on the fault surface and the displacement sense of the fault (Appendix H). These 266 data points were used to perform statistical analysis and to calculate the orientations of paleostress and paleostrain axes (Fig. 9). The sense of displacement on the fault planes was established using criteria for sense of displacement for brittle rocks outlined by Pettit (1987).

Characteristics used to distinguish fault systems include strike and dip, sense of movement, continuity along strike, crosscutting relationships among faults and time relationship with respect to mineralization and igneous rocks, and the style of faulting. The style of faulting indicates the differences between fault zones and discrete faults. Fault zones are characterized by thick zones (>50 m) of brittle cataclastic deformation and by the transitional contact with the non-faulted rock. Discrete faults refer to thin (<2 m) continuous faults/fracture zones in sharp contact with non-faulted rock (Figs. 6 and 8). Based on the above conditions, four main fault systems are distinguished at the Escondida deposit (Table 1).

Fault	Fault Zone	Strike	Dip	Sense of	Mineralization		Comments
System				Movement	Stages 1&2	Stage 3	
NNW	Zaldivar	N10°-20°W	>70°W	S	Yes	Weak	Fault zones
	Panadero	N10°-20°W	75°–85°W	S	Yes	Weak	formed by thin,
	Ortiz	N10°-15°W	75°–85°W	S	Yes	Weak	interconnected
	Portezuelo	N10 [°] -20 [°] W	78°–85°E	S	Yes	Weak	NW faults
	Ferrocarril	N10°-20°W	>70°W *	Unknown	Yes	Weak	
Cerritos		N40°-60°W	65°S	S	Yes	Weak	
Enargita		N40 ° -75 °W	70°–88°N	S & D	No	Yes	
El Agua		N60°-75°E	60°–70°S	D	No	Weak	

Table 1. Main fault systems of the Escondida deposit.

"S" = sinistral, and "D" = dextral. Asterisks indicate interpreted dip.



Fig. 8: Structures of the Escondida open pit. After Veliz and Padilla, 1997.

<u>NNW Fault System (Zaldivar, Panadero, Ortiz, Portezuelo, and Ferrocarril Fault</u> <u>Zones)</u>

Five NNW-striking mineralized fault zones are recognized at Escondida: the Panadero, Ortiz, and Portezuelo zones within the open pit (Fig. 8); and the Zaldivar and Ferrocarril faults zones outside of the present pit (Fig. 6). The average strike of these mineralized fault zones is N10°W, with variations between N20°E and N20°W. Faults located in the western part of the pit dip eastward, whereas those in the eastern part of the pit dip westard (Fig.8). The N10°W-striking fault zones are characterized by brittle cataclastic deformation, 50 to 250 m in width. Individual fault planes within fault zones are identified as having continuous planes with a thickness up to 0.5 m of fractured rock or gouge. These individual planes present undulating surfaces along their strike and dip. The maximum continuity of individual fault planes parallel to the main strike is less than 1,000 m, but the continuity of the fault zones persist with parallel structures (Fig. 8). In some instances the limits of these main fault zones are clearly defined by sharp transitions from strongly broken and altered rock to a less-altered rock. However, their limits are normally gradational and include a series of faults parallel to the main zone and a series of WNW-striking cross faults or stepover faults. The association of the main NNW-striking and the secondary WNW-striking structures form rhombic geometries within the fault zones. The less continuous WNW-striking faults are mineralized and strike between N20°W and N70°W. The dips of these faults shallow out as they approach the main N10°W-trending fault planes.

The principal N10°W-striking faults exhibit continuities up to 1,000 m within the andesites, but their continuities decrease in the intrusive rocks. For example, faults of the

Ortiz Fault Zone (Figs. 6 and.8) are continuous in the andesites near the contact with the Escondida stock. However, within the central part of the stock, the faults of this fault zone become discontinuous. At the eastern contact of the Escondida stock with the andesite, the Ortiz Fault Zone forms, in plan view, a rhombic-shaped fracture zone approximately 700 m long and 200 m wide. The vertical geometry of this rhombic structure can be observed in the southeastern wall of the open pit where the fracture zone narrows down, so that the cross section of the fault zone displays a flower-structure geometry (Woodcock and Schubert, 1994).

NE Discrete Faults (El Agua System)

El Agua faults strike ENE, dip between 60° and 70° south, exhibit a dextral sense, and occasionally contain sulfides of the late advanced argillic event. They appear to represent the main pathways of water in the present open pit. These faults may show strike persistence greater than 2,000 m (Fig. 8).

The NE faults are characterized by a series of continuous faults comprising a highly fractured zone with sharp contacts, red clay gouge or brecciated sulfides of the late advanced argillic hydrothermal event. The fractured clay gouge zones normally do not exceed 0.5 m. Recognized displacements along these faults are less than 50 m in a dextral-lateral sense. At the regional scale, lineaments of this orientation are observed in satellite images even in areas covered by Miocene gravel.

NW Discrete Fault Systems (Enargite and Cerritos Systems)

The Enargite System. Faults of the Enargite fault system are characterized by a series of thin (<2-m-thick) continuous faults comprising a highly fractured zone with sharp margins and mineralization from the late advanced argillic event and from earlier

mineralizing events. The thickest and most continuous veins contain mainly sulfides of the late advanced argillic hydrothermal event. Faults of the Enargite system exhibit a sinistral sense of displacement along northwest-striking faults that dip between 70° to 89° north (Fig.8). The majority of late pebble dikes, and the most continuous late barren granodioritic dikes, also present a N20°–40°W preferential orientation (Fig. 8).

The Cerritos System. Faults of the Cerritos system are NW-striking, but are clearly different from the main NW faults. They exhibit left-lateral displacement along N60°W- to N70°W-striking faults that dip approximately 65° south (Fig. 8). They are less than 20 cm thick and commonly contain sulfides from the quartz-sericite and potassic hydrothermal events and only rarely host sulfides from the late advanced argillic event. These faults undulate along strike and dip and occur mainly at the northern margin of the Escondida stock.

Steeply dipping fault planes and shallowly plunging slickenlines suggest that all the fault systems described above are related to the dominantly transcurrent regional Domeyko Fault System. Late, normal-vertical reactivation along NNW- and NWstriking faults has displaced the enrichment blanket from 10 to 50 m.

Orientations of paleostress were calculated using the software Brute 3 (Hardcastle and Hills, 1991), a grid search method that calculates the best-fit orientations for $\sigma 1$, $\sigma 2$, and $\sigma 3$. The program uses a datafile containing the strike and dip of each fault plane, the rake and plunge of slickenlines, and the relative sense of motion along each fault. Paleostrain calculations were completed using the software FAULKIN (Allmendinger et al., 1993) that uses a graphic method to calculate the infinitesimal principal shortening (P on Figs. 9c and 9d) and extension (T on Figs. 9c and 9d) axes, which may, but do not have to, coincide with the principal stress directions (Allmendinger et al., 1989). Figure 9 presents the calculated directions of paleostress and the estimated directions of paleostrain associated with the dominantly sinistral movement of the mineralized faults and the post-mineralization dextral movements along the NE fault system. These data indicate a NW-SE axis of maximum compressive stress for mineralized faults, and an ENE-WSW principal compressive stress axis for the post-mineralization dextral movements along the NE faults.

Interpretation and Discussion

The data indicate that the Escondida porphyry copper deposit was developed in an extensional zone formed along strike-slip faults of the regional Domeyko Fault System.

At the district scale, the geometry of faults presented in Figure 5 suggests a dextral sense of movement for a transcurrent fault system. However, the sense of movement observed in fault planes is mainly sinistral. One possible explanation for this discrepancy is that there was an early dextral sense of movement associated with the development of the geometrical arrangement of faults observed at the district scale (Fig. 5) and a subsequent sinistral sense of movement associated with emplacement of the Escondida stock. The following paragraphs describe a possible structural evolution model for the Escondida deposit within a sinistral transtensional structural environment.

At Escondida, the development of the sinistral mineralized north-northweststriking fault systems is interpreted to be synchronous with the emplacement of all the intrusive rocks mapped in the deposit and with the evolution of the hydrothermal system. The dextral displacement on some of the NW faults and all the NE faults is interpreted to postdate the emplacement of intrusive rocks and alteration-mineralization. The NE fault system probably formed late in the evolution of the magmatic-hydrothermal system.

Dynamic and kinematic analyses of the mineralized fault system indicate a maximum stress direction of N39°W and a direction of minimum stress of N50°E (Fig. 9). Fault geometries of the mineralized system are consistent with a simple shear model in a transcurrent environment as follows: 1) The north-northwest-striking faults represent the principal deformational zone (PDZ, Fig. 10); 2) The west-northwest-striking faults are interpreted as secondary (R, R') and tensile (T) structures (Fig. 10); 3) Faults located at angles between 10° and 20° from the PDZ are synthetic (R) structures; and 4) Faults at angles greater than 65° from the PDZ seem to be in antithetic (R') orientation; however, their sense of movement is sinistral, which is not consistent with the simple shear model. This kinematic inconsistency may be due to late reactivations associated with the activity of the post-mineralization faults. The preferential west-northwest strike of mineralized veins, the Escondida stock, pebble dikes, and late barren dikes are coincident with the position of tensile (T) and secondary (R,R') structures. In an ideal model, Reidel structures would be closed and only affected by shearing. However, the tendency of Reidel fractures to behave as a combination of shear and extensional fractures could have been facilitated by high pore fluid pressure and by fault rotation.

I propose that the Escondida porphyry system was formed during the coeval evolution of a transcurrent fault system and the injection of magmas into a tensional gash



Fig. 9: Rose diagrams, P and T axes directions, and paleostress orientations of structural data from the Escondida deposit. A. Diagram showing all fault systems; B. Quartz-sericite and advanced argillic mineralized veins, pebble dikes, and late barren dikes; C. P and T axes directions and paleostress orientations of the mineralized fault system; D. P and T axes directions and paleostress orientations of the post-mineralization fault system. P-T axes were calculated with the software FAULKIN (Allmendinger, et al., 1993). Paleostress orientations were calculated using the fault inversion software Brute 3 (Hardcastle and Hills, 1991).

developed between the Ferrocarril and the Panadero-Ortiz fault zones (Fig.10). The geometry of the faults and the position of the Escondida stock are interpreted as a stepover between these two sinistral strike-slip faults (Fig. 10). In a left-lateral displacement environment, the area of the stepover would have been under extensional conditions (Fig. 10). Therefore, as expected by the Coulomb failure theory (Davis and Reynolds, 1996), a tensile zone formed perpendicular to the least principal stress (σ_3) and later rotated, forming a cymoidal final geometry (Fig. 10). It is probable that the main NW-striking shear zones (Zaldivar, Panadero, Ortiz, Portezuelo, and Ferrocarril) facilitated the upward movement of a buoyant magma. Once this magma reached the tensile gash in the upper crust, the magma volume was initially oriented in a NW-SE direction, roughly parallel to the stepover and to the orientation of the maximum principal stress (σ_1) and maximum shortening calculated for the mineralized faults. The magma then expanded in the N50°E direction parallel to the axis of maximum extension and least principal stress (σ_3). This combination resulted in the N40°W elongated shape of the Escondida intrusive stock (Fig. 10).

The contacts of the intrusive rock and the andesitic host rock are sharp, and xenoliths of andesite are uncommon within the Escondida stock. This lack of xenoliths may reflect a passive intrusive process, perhaps facilitated by the sub-horizontal position of the least principal stress (σ_3) within a strike-slip environment, allowing the expansion of magma in the northeast direction. Generally, tensile gashes are observed at small scales associated with strike-slip faults (Woodcock and Schubert, 1994). The long length and wide separation of walls of the tensional gash are proposed as a structural control of



Fig. 10: Structural interpretation of the Escondida deposit. a. Main structural elements and the shape of the Escondida stock at 2,800 m.a.s.l. (patterned). b. Ideal simple-shear left-lateral strike-slip zone and Reidel shear array (Davis and Reynolds, 1996); R is synthetic; R' is antithetic to main movement on the principal displacement zone (PDZ, dashed line); P, late synthetic shear fractures; T, tensile fractures (patterned rectangle). c. Plan view projection of strain ellipsoid with the calculated orientations of S₁ and S₃ within a sinistral N10°W shear zone, and the simplified shape of the Escondida stock in plan view.

the Escondida stock. They were probably sustained by the injection of magma and aqueous fluids that kept the pore fluid pressure high during the development of the porphyry system, facilitating the formation and growth of tensional structures. The northwest-southeast maximum principal stress orientation was active at least from the earliest stages of veining to the latest stages of post-mineral dikes.

Strike-slip structural fault zones are characterized by the presence of compressional and extensional conditions at the same time (Fischer, 1985; Woodcock and Schuber, 1994). This situation generates differential pressure in the upper crust that may facilitate the movement of magmas and aqueous fluids, sometimes resulting in the development of magmatic-hydrothermal systems. Sibson (1989) proposed a mechanism that he called fault-valve behavior, suggesting that earthquakes trigger the movement of aqueous fluids to low-pressure areas within fault zones. Other authors have investigated the emplacement of plutons and hydrothermal systems along strike-slip faults (D'Lemos et al., 1992; Monrand, 1992; Paterson and Fowler, 1993). The model proposed in this study is limited by very little data in the vertical dimension. Additional structural studies in the Escondida district and other mining districts located along the Domeyko Fault System could add to our knowledge of the processes that control the shallow emplacement of hydrous magmas associated with the development of porphyry systems along strike-slip faults.

Paragenesis and Zoning of Hydrothermal Minerals, and Distribution of Supergene Minerals <u>Hydrothermal Alteration</u>

Introduction. At Escondida, both time and space must serve as bases to understand the alteration process. Overprinting of both pervasive and vein-veinlet alteration by younger alteration types marks the style of evolution. The alteration process was dynamic, not static; consequently, rigorous definitions of zones and stages of alteration must incorporate the reality of sequential evolution. Stages are used in this paper to group alteration effects in time, and zoning is used to indicate the distribution of mineral associations in space. Sulfide assemblages also vary with each hydrothermal stage; they are described in the next section.

The study and description of deep hypogene hydrothermal features are complicated by the high-level, deeply-penetrating effects of a late advanced argillic event and by a deep supergene overprint. The hypogene alteration types considered below were determined from drill holes penetrating below the supergene and advanced argillic zones (Figs. 12 and 13) and from relics of hypogene alteration within the open pit. Different alteration mineral assemblages are not necessarily exclusive to recognized zones of alteration. Figure 11 shows the distribution of alteration zones. Despite the dynamic evolution of the system, three main stages of alteration, here designated Stage A, B, and C, are defined based on mineral associations and their mode of occurrence in space and time (Table 2).

The effects of the early, or Stage A, processes are seen in both pervasive alteration styles and in alteration of some stockwork veins and veinlets. Two pervasive alteration types are present in Stage A. These were synchronous and are interpreted as

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manifestations of the earliest stages of intrusive igneous activity. The mafic phenocrysts and the groundmass of the andesite wall rock of the porphyry complex have been extensively, and locally completely, altered to biotite. Although affected by later hypogene alteration, weathered, and modified by acid supergene effects, these biotitealtered rocks were still conspicuous in pit benches in 1998. At the contact of the intrusion with the volcanic rock, a second kind of pervasive alteration has taken place and is manifested by texturally destructive silicification, which has affected both rock types. Another type of pervasive alteration is represented by replacement of orthoclase in the groundmass of the Escondida intrusive stock. Drill-hole data beneath supergene alteration indicate that local volumes, on the order of cubic meters, of the intrusive rock have been pervasively altered to orthoclase, although much of the orthoclase alteration is seen in proximity to stockwork veins. The transition between pervasive and veincontrolled alteration is marked in the rocks of the mineralized center of the deposit by discontinuous veins of quartz and quartz-orthoclase.

Propylitic alteration as defined at Escondida is characterized by sporadic conversion of plagioclase to grossularite and more commonly to epidote and montmorillonite; by conversion of hornblende and biotite to chlorite; by albitization of plagioclase; and by the presence of widespread carbonate and zeolite veins. The conversion of plagioclase to grossularite was probably synchronous with the development of biotite alteration in the andesite and orthoclase in the intrusive rock. Propylitic alteration surrounds the center of mineralization and its attendant early potassic alteration. The early, or Stage A, alteration was followed by the formation of alteration in selvages adjacent to stockwork veinlets. This alteration is separated into two successive mineral associations, chlorite-sericite±quartz, and quartz-sericite. The advanced argillic assemblage represents the latest alteration stage. Development of advanced argillic alteration took place late in the life of the system, when high-level fracture permeability had developed and progressed through the time of fracture formation, as indicated by the presence of quartz-enargite-pyrite-chalcopyrite-bornitesphalerite-covellite-chalcocite and sericite-pyrophyllite-alunite veins crosscutting the pervasive assemblage at high level. Albite rims are observed in thin-section and in electron-microprobe analysis of plagioclase as growth zones around plagioclase in rocks of the propylitic zone and in samples with strong quartz-sericite alteration. These occurrences are sporadic and not obvious at hand-specimen scale; therefore, it was not possible to establish the time and space placement of this event.

Ojeda (1986) and Alpers and Brimhall (1988) reported a group of K-Ar ages of hydrothermal biotite and sericite ranging between 33.7 ± 1.4 Ma and 31.0 ± 1.4 Ma with two other samples of 38.3 ± 3.0 Ma and 39.1 ± 2.2 Ma. The authors suggested, therefore, that the hydrothermal evolution at Escondida took place between 33.7 ± 1.4 Ma and 31.0 ± 1.4 Ma, dismissing the two older ages by arguing possible contamination and disagreement with the rest of the data. However, Richards et al. (2000) propose a 37.9 ± 1.1 Ma age for the hydrothermal system at Escondida, coeval with the emplacement of the Colorado Grande intrusion. Richards et al. (2000) also suggest that the K-Ar ages reported by Alpers and Brimhall (1988) and by Ojeda (1986) may represent the time of

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Fig. 11: Plan view showing dominant hypogene alteration mineral associations. From 100 to 650 m below surface. Compilation from drill hole information and the geology of the open pit. Mt = magnetite, Bn = bornite, Cpy = chalcopyrite, Py = pyrite, Mo = molybdenite, Sp = sphalerite, Gn = galena, Enar = enargite, Bt = biotite, Garn = grossular, Epid = epidote, Kfds = orthoclase, Qz = quartz, Chl = chlorite, Ser = sericite, Cal = calcite. After Padilla et al., 2001.



Fig. 12: Section N-S 16450, looking west. See figures 5 and 11 for symbols and location. Dominant mineral alteration is outside parenthesis and subordinated mineral alteration in parenthesis. High and low enrichment are subdivisions of the chalcocite blanket. High-enrichment zone does not contain pyrite. Low-enrichment zone contains a few percentage of pyrite coexisting with the supergene copper sulfides. From Padilla et al., 2001.



Alteration



Mineralization



Fig. 13: Section N-S 15100, looking west. See figures 5 and 11 for symbols and location. Dominant mineral alteration is outside parenthesis and subordinated mineral alteration in parenthesis. High and low enrichment are subdivisions of the chalcocite blanket. High-enrichment zone does not contain pyrite. Low-enrichment zone contains a few percentage of pyrite coexisting with the supergene copper sulfides. From Padilla et al., 2001.

emplacement of the rhyolite that reset the original K-Ar system. A detailed review, based on new Ar/Ar and U/Pb data, of the geochronological evolution of the magmatic-hydrothermal system is discussed further in Chapter 4.

The temporal evolution of alteration reported here as stages is best documented by the overprinting of mineral associations and by crosscutting relationships of veins. The "intensity of fracturing" notations of this study follow from the work of Titley and Heidrick, (1978): weak intensity, 0.2 cm^{-1} ; moderate, 0.5 cm^{-1} ; and intense, $>1.0 \text{ cm}^{-1}$. In the following description of alteration, the terms intense, moderate, and weak alteration are used for the megascopic description of rocks. Intense alteration refers to rocks with their original mineral texture completely obliterated by alteration; exceptions include primary quartz grains apparently unaffected by hydrothermal alteration of any type, and relic plagioclase grains in andesite altered to the biotitic assemblage. Moderate alteration is a term for rocks where, in spite of almost complete hydrothermal alteration of individual mineral grains, the main textural characteristics of the rock can still be recognized. The term weak alteration describes rocks with mainly fresh characteristics but also with patches where alteration effects are recognizable with a hand lens.

Detailed Description of Hydrothermal Alteration.

Stage A—Potassic. Potassic alteration shows lithological control. In the Escondida stock, early potassic alteration is represented mainly by weak, disseminated K-feldspar that replaces plagioclase crystals and groundmass of the intrusive rock, giving a pink tint to the rock (Figs. 14e and 14g). Biotite crystals of the intrusive rock are magnesium rich (X(phl) 0.6/X(ann) 0.23/X(sid) 0.17), and their F/OH-Mg/Fe relation

(Fig. 15) suggests that they were re-equilibrated by the hydrothermal event (Ague and Brimhall, 1988).

In andesite, potassic alteration is characterized by secondary biotite with minor amounts of disseminated and vein-controlled K-feldspar and anhydrite (Figs. 14d, 14f, and Table 2). The area of biotitic-altered andesite is semi-elliptical and changes outward to propylitic alteration (see below) and inward either to K-feldspar-altered intrusive rock or to chlorite-sericite in the same andesite (Fig. 11). Most of the biotite is fine-grained (<0.1mm diameter) and replaces minerals in the groundmass of the rock and the mafic and plagioclase phenocrysts; however, the largest plagioclase phenocrysts are only partially affected by this alteration. Biotite crystals are magnesium rich (X(phl)0.54 /X(ann) 0.22 / X(sid)0.23), and their F/OH-Mg/Fe relation plots in the transition between hydrothermal biotite and igneous biotite from a weakly contaminated I-type pluton (Fig. 15; Ague and Brimhall, 1988). In hand samples, andesite with this type of alteration has a characteristic black color, and the preservation of plagioclase ghosts now altered to montmorillonite reveals the original texture of the rock (Fig. 14d).

Stage A—Propylitic. Propylitic alteration is defined here by the development of assemblages containing epidote with minor amounts of chlorite, montmorillonite, biotite and grossularite, and widespread carbonate and zeolite veins (Fig. 11 and Table 2). These alteration minerals replace amphibole and plagioclase in andesite. Grossularite is found only replacing plagioclase (Figs. 14a and 14c). Some plagioclase crystals reveal an albitic halo. This propylitic alteration forms a halo around the potassic zone and is mainly pervasive with occasional partial or total destruction of the original mineral grains and texture of the andesite (Fig. 14b).

Stage A—Silicification Shell. A shell of silicified rock, which is present at the contact between the andesite and the Escondida stock, is interpreted to represent a contact metasomatic phenomenon. This silicification shell has a width that varies between 20 and 40 m that affects both the andesite and the Escondida intrusion. This silicified zone is not shown in figures 11, 12, and 13 because it is too narrow to be seen at the scale of these maps. The silicified rock is aphanitic, hard, and strongly fractured. In thin section, the rock consists of an aggregate of fine-grained quartz with grain sizes smaller than 50 μ m. The silicified zone represents one of the earliest alteration events and is cut by veins associated with all alteration assemblages described below. The zone has been recognized in the present pit, but its continuity along the stock contact has not yet been revealed.

Stage A—Early Veins. The earliest veins contain quartz or quartzorthoclase±biotite±anhydrite. The best samples of veins from the early stage were found in the northwestern part of the deposit and in deep drill holes. Moreover, relics of those veins are found throughout the deposit, normally reopened and filled by vein minerals deposited during later events. Veins of the early stage are subdivided into three subgroups:

A1. Discontinuous strongly sinuous-curved quartz veins without alteration halos that occur mainly in the intrusive rock, but also in andesite located near the contact with

Fig. 14: Hydrothermal Stage A of the Escondida deposit. Photos of hand samples and thin sections.

- a) Plagioclase replaced by garnet (grossular) in andesite.
- b) Epidotization of andesite.
- c) Grossular replacing plagioclase in andesite.
- d) Andesite with pervasive biotitization (NQ core).
- e) Slab of the Escondida stock cut by sinuous quartz veins, which in turn are cut by biotite-anhydrite-K-feldspar veins.
- f) Photomicrograph of andesite with pervasive fine-grained biotite alteration cut by veins of K-feldspar and quartz.
- g) Photomicrograph of quartz+K-feldspar and K-feldspar-only veins cutting a plagioclase crystal of the Escondida stock.
- h) Reflected light photomicrograph of the characteristic opaque assemblage of hydrothermal Stage A: magnetite (Mt) + bornite (Bn)+ chalcopyrite (Cpy). Covellite is in the photo but it is not common within Stage A.









Fig. 14



1 cm



the intrusive rock. Their boundaries against the host rock are irregular but well defined. They are generally no longer than 10 cm and vary between 1 mm and 2 cm wide.

A2. Continuous quartz veins without alteration halos that occur mainly within the intrusive rock. The walls of these early stage type A2 veins are irregular but well defined. They are up to 70 cm long and less than 1 cm to 5 cm wide. This group of early veins shows multiple events of emplacement.

A3. Veins formed of quartz-K-feldspar plus minor amounts of biotite and anhydrite (Fig. 14e). Such veins are more continuous and less sinuous than type A1. They are characterized by pink K-feldspar-alteration-halo selvages that make the vein margins irregular and poorly defined. The vein widths range between 1 mm and 3 cm.

Type A3 veins postdate types A1 and A2 veins in most instances. Biotite from the early veins is the most magnesium-rich of the system (X(phl)0.66 / X(ann)0.22 / X(sid)0.12), and their F/OH-Mg/F data fit within the hydrothermal field of porphyry copper systems (Fig. 15; Ague and Brimhall, 1988).

Stage B—Chlorite+Sericite+Quartz. The width of this zone varies from 1 to 2 km and it is open at both the northeastern and the southeastern limits of the deposit (Fig. 11). Disseminated and vein-controlled chlorite-sericite alteration overprints the biotite-altered andesite (Figs. 14d and 17b). In the Escondida stock, Stage B is represented by selective alteration of biotite and other mafic minerals, by the alteration of K-feldspar of the potassic assemblage to chlorite-sericite, and by the introduction and precipitation of smaller amounts of chlorite in cracks of reopened Stage A veins. The original textures of the andesite and the intrusive rock are preserved, except in the center of the veins or in



Fig. 15: Comparison of hydrothermal biotite from the porphyry deposits of Escondida, Butte, Santa Rita, W-deposits, and Mo deposits, and igneous biotite compositions.

Symbols indicate biotites from Escondida. I-SCR represents plutons strongly contaminated and reduced by the assimilation of reduced sediments. I-WC to I-SC are plutonic rock types from weakly to strongly contaminated magmas, formed by interaction of mafic I-type magmas derived from the upper mantle with continental crust components. Modified after Ague and Brimhall (1988).



Fig. 16: Mg-Fe composition of dark and white sericites from the Escondida deposit.

the first few millimeters of the their alteration halos. Toward the outer limit of the chlorite-sericite zone—mainly in andesite—chlorite is more abundant than sericite, but sericite is more abundant in the rocks closer to the stock (Fig. 11). In hand specimens, chlorite-sericite alteration is characterized by its dark-green to pastel-green color.

Veins associated with the chlorite-sericite alteration of Stage B are named here as type B1 veins. These veins cut or reopen the early veins described above. They have lengths that vary from a few centimeters up to 50 cm, and they are normally thin, with thicknesses ranging from less than 1 cm to 3 cm. The type B1 veins of chlorite-sericite assemblage are more continuous than the veins associated with the potassic alteration, but their margins with the host rock are nonetheless irregular and diffuse. They may be sinuous and show "branching" habits. In andesite, type B1 veins show zoning that starts with a <1cm wide vein-filling formed by sulfides with or without minor amounts of quartz grains smaller than 50 μ m. From the center, the alteration halo consists of a mixture of sericite and subordinate chlorite that changes outward to mainly dark-green chlorite with subordinate sericite (Figs. 17c and 17d).

Stage B—Quartz-Sericite. The quartz-sericite assemblage is the main alteration type in the center of the deposit, and it affected the southeastern portion of the Escondida stock and the andesite close to the contact with the intrusive rock (Fig. 11). This mineral association occurs mainly in veins and in their alteration halos. In hand samples this alteration is characterized by a mix of colors including pastel green, dark gray, and white (Figs. 17a and 17e). Where this alteration is very intense, the rock is converted to a



a) Hand sample showing chalcopyrite-pyrite veins with dark-sericite halos. Sulfides are within the veins and disseminated in the the alteration halo. The rock is the first intrusive phase (crowded).



b) Hand sample showing andesite with strong chlorite-sericite alteration (green) and a 1 mm vein of chalcopyrite with thin sericitic halo (white). Patches of black color are remnants of biotitic alteration.



c) Photomicrograph showing andesite with chlorite-sericite alteration under plane-polarized light. Sericite occurs mainly at the margin of the sulfide vein (white), while chlorite (green) is more abundant away from the vein.



d) Photomicrograph of thin section from sample of andesite with chlorite-sericite alteration under cross-polarized light. Chalcopyrite crystals occur along the vein and are disseminated within the altered rock.



e)Hand sample showing on the right side early veins with chalcopyrite that are cut by a pryrite white-sericite vein (on the left side of the photo).



f) Photomicrograph of a crystal of chalcopyrite in the middle (black) surrounded by dark sericite alteration. Plane-polarized light.

Fig. 17: Photos of hand specimens and thin sections from Stage B veins.

white, mesoscopically textureless mass in which the intrusive rock can be distinguished only by preserved quartz phenocrysts. The density of veining in this zone is intense.

Veins associated with quartz-sericite alteration are named type B2. They are usually longer than 20 cm and in some cases longer than 1 m, with alteration halos that vary from less than 1 cm up to 15 cm and with irregular outer limits that grade from intense to moderate to weak. The vein-fillings consist of quartz and sulfides with alteration selvages formed by texturally destructive sericitic alteration. Outward, this alteration continues, but with less intensity and preservation of plagioclase and orthoclase phenocryst shapes.

In the outer vein halo, the tabular feldspar crystals are altered to sericite and are surrounded by a fine-grained pale-green sericite aggregate. Green sericite have higher contents of Fe and Mg than the white sericite. In Figure 16 the lowest Fe and Mg values of white sericite are 0.4 and 1 weight percent oxide, whereas the dark sericite has Fe and Mg as high as 2.2 and 3.2 weight percent oxide, respectively.

Stage C—Advanced Argillic. The last hydrothermal stage of alteration at Escondida is represented by the acid-sulfate assemblage that affects the andesite and the Escondida intrusion. This is also the only known hypogene alteration that affects the rhyolite. The distribution of this alteration is controlled by the main fault zones and by the contact between the rhyolite and the country rock. In Figure 11, the spatial distribution of advanced argillic alteration was determined by locating more than 200 composite samples that were analyzed by X-ray diffraction by Alpers and Brimhall (1988) and this work. The parageneses associated with this late-acid event were



a) Hand sample showing a late pyrite vein with black color due to chalcocite coating. The margins of the vein consist of banded quartz, and within the vein are white spots of illite.



b) Microphoto showing a fragment of pyrite surrounded by chalcopyrite that is replaced by covellite.



argite (pinkish) and phalerited) Photomicrograph showing bands of covellite (blue) after chalcopyrite (yellow).

20 un



e) Hand sample showing pyrite (yellow) and alunite (white) from a sulfide rich vein.



f) Photomicrograph showing supergene chalcocite in fractures and surrounding pyrite (light yellow) and chalcopyrite (dark yellow).

Fig. 18: Photos of hand and thin samples from the late advanced argillic hydrothermal stage.

Mineral Assemblages Main Characteristics of Veins Comments **Propylitic** Total content of sulfides with the Veins of Stage A represent the Pervasive and vein-veinlet alteration transition between early pervasive potassic assemblages < 0.5 vol. including epidote-chlorite-zeolites± and later vein-veinlet alteration %, with hypogene copper grades pyrite and rarely chalcopyrite, styles. ≤ 0.2 wt. %. Veins A1 and A2 are S grossular, and albite. Probably similar to A veins described at t started during Stage A and evolved Veins A1: sinuous and discontinuos the El Salvador, whereas A3 veins during the development of stages B barren quartz veins. Affecting the are similar to B veins from the El a and C. Affecting andesite. Salvador deposit. However, no granodiorite. g Silicification molybdenite has been observed e Pervasive fine-grained silicification Veins A2: Ouartz veins with no with these veins at Escondida. shell at the contact intrusive rockalteration halo. More continuous veins than A1. With chalcopyrite A andesite host rock. Interpreted as and bornite. Affecting the contact effect during the emplacement of the Escondida stock. granodiorite. Veins A3: irregular; but more

ahle 2	Characteristics	of the three	main hy	vdrothermal	stage
abit 2.	Character istics	or the three	main ny	y ui othti mai	stage

		1	0
20	Pot	tassic	
~38 Ma	•	Pervasive fine-grained biotite with minor orthoclase affecting the andesitic host rock. Magnetite-bornite-chalcopyrite	Veins A3: irregular; but more continuous than A1 veins. Center and halo formed by orthoclase+quartz +biotite-anhydrite. With bornite-
	•	Pervasive but mainly vein- controlled orthoclase+quartz ±biotite-anhydrite. Includes bornite-chalcopyrite. Mainly affecting the Escondida stock	chalcopyrite. Mainly affecting the granodiorite; less extensive in andesite.

Chlorite-Sericite±Quartz Vein controlled alteration, affecting

biotitic-altered andesite. In the intrusive rock, chlorite selectively altered mafic minerals and S sometimes orthoclase. Within the intrusive rock, chlorite also occurs in t < 1mm cracks that cut veins from a Stage A. Chalcopyrite±pyriteg molybdenite. e Quartz-Sericite (greenish-grayish) Vein controlled alteration mainly within the intrusive rock and stronger B along fault zones. Sericite in halos presents pale-green to gray colors. Associated sulfides are ~38 chalcopyrite±pyrite-molybdenite .

Ma **Pyrite-Sericite (white)** Vein-controlled alteration formed of pyrite±chalcopyrite and strong halos of white sericite and disseminated pyrite.

S **Advanced Argillic**

- t Pyrophyllite-sericite-quartz-alunite
- a with abundant sulfides including
- g e bornite-chalcopyrite, pyrite, lamellar
- covellite, minor amounts of
- chalcocite, enargite, sphalerite with С
- exsolutions of tennantite and 36
- chalcopyrite, and galena. Pervasive x
- at the contact of rhyolite with its host 34
- rock, but its main occurrence is in $N40^{\circ}W$ veins within major fault Ma zones.

Veins C:

Veins B1:

molybdenite.

Veins B2:

Veins B3:

Associated with the chlorite sericite

veins (<5 mm) with quartz absent or

assemblage, there are thin sulfide

sericite-chlorite with sulfides that

minor. Alteration halos are of

grade outward to dominantly

include chalcopyrite±pyrite-

chlorite, replacing biotite in the

biotitic-altered andesite. Sulfides

Within the sericite-quartz assemblage

with thick quartz-sericite (pale-green

and gray) halos. Associated sulfides

are chalcopyrite±pyrite-molybdenite.

event, there are pyrite± chalcopyrite

veins with white sericite-pyrite halos.

Associated with the last sericitic

veins are formed by quartz-sulfide

Continuous veins, up to 2 m wide. Banded internal textures starting with quartz, followed by pyrite-enargite, pyrite-bornite-chalcopyrite, pyritesphalerite-chalcopyrite-tennantite, covellite-chalcocite- enargite, pyritegalena, and alunite.

Veins of Stage B are irregular and less sinuous than the veins of Stage A. Very often veins of Stage B reopened veins of Stage A. Bornite and magnetite are no longer present in this stage, whereas molybdenite and pyrite appear for the first time in the porphyry system. Sulfide content increases to 2 vol. % with chlorite-sericite and quartzsericite (greenish-gravish sericite), with pyrite:chalcopyrite ratio of 1:3. With the white sericite-pyrite event, total content of sulfides can go locally to 5 vol. % with a pyrite:chalcopyrite ratio of up to 10:1. Where this stage is strong, Cu grades vary between 0.4 and 0.6 wt. %. Vein types similar to B2 and B3 were classified as D veins at the El Salvador deposit

This is the only stage that affects the rhyolite. Veins normally do not include the whole paragenetic sequence of sulfides. More often, veins include only pyrite with minor amounts of enargite, covellite, and alunite. Similar veins were classified as D veins at the El Salvador deposit.

established on thin and polished sections; however, there has not been a detailed mineralogical study of the distribution of sulfides, sulfates, and silicates of the advanced argillic event. Assemblages belonging to this alteration type include sericite, pyrophyllite, kaolinite, alunite, and quartz. Banded quartz veins are present, and sulfides are abundant (Fig. 18a). In the contact between the rhyolitic dome or dike and the andesite, this alteration is pervasive and has a characteristic mottled texture as a result of white, pyrophyllite-sericite spots.

Veins of Stage C vary from a few millimeters up to 1 or 2 m thick, and have banded, massive, and breccia texture (Figs. 18a and 18b). They include at least two different types of euhedral quartz and abundant sulfides with minor amounts of alunite. Locally, the vein-fill of these veins is brecciated and cemented with alunite. At the margins, bands of fine-grained sugary quartz (up to 500 μ m in diameter) and semitranslucent fine-grained quartz (<70 μ m in diameter) have thicknesses between <1 cm and 10 cm.

Mineralization

Introduction. Ore minerals in the Escondida deposit are grouped into three main ore types: hypogene sulfides, supergene sulfides, and copper oxides. Using a 0.3 weight percent Cu cutoff, 49 weight percent of the total tonnage is hosted by the Escondida stock, with a copper grade of 1.12 weight percent, which represents 59 weight percent of the total fine copper resource. The other 51 weight percent of the total tonnage is hosted by the andesite, with a copper grade of 0.75 weight percent, which constitutes 41 weight percent of the total fine copper resource (Table 3).

Rock type	Proportion of rock in orebody (wt %)	Cu grade	Proportion of total Cu (wt %)
	(112 /0)	(117,0)	(112 70)
Porphyry	49	1.12	59
Andesite	51	0.75	41
Total	100	0.9	100

Table 3. Total mineralization by rock type, Escondida deposit.

Table 4. Total mineralization by rock and ore type, Escondida deposit.

Rock Type						
	Andesite Porphyry					
Ore type	Proportion of ore type in orebody	Cu grade by ore type	Proportion of total Cu by ore type	Proportion of ore type in orebody	Cu grade by ore type	Proportion of total Cu by ore type
	(wt %)	(wt %)	(wt %)	(wt %)	(wt %)	(wt %)
High enrichment	25	1.06	39	29	1.39	44
Low enrichment	17	0.69	18	27	0.96	28
Primary	42	0.54	34	34	0.66	25
Cu oxides-mixed	16	0.57/0.35	9	10	0.59/0.37	3
Total	100		100	100		100

Resources in these tables were calculated using the drill hole data available in 1997 and a cutoff of 0.3 weight percent copper.
Detailed Description of Mineralization.

Hypogene Ore. The hypogene mineralization represents 30 percent of the currently calculated and discovered total copper resource at Escondida and is mainly present in the deepest parts of the deposit or at its margins, but some occurs as relic volumes within the supergene blanket. The three main hydrothermal alteration stages described above also contain different Cu-Fe mineral associations (Table 2). Early stage, magnetite-bornite-chalcopyrite ore (Fig.14h) is associated with biotite and K-feldsparquartz alteration and has a content of sulfides lower than 0.5 volume percent. At microscopic scale, veins of Stage A are commonly seen to be reopened, or crosscut, by younger stages. Within Stage B veins, chalcopyrite with minor amounts of molybdenite and pyrite are intergrown with sericite or chlorite-sericite (Figs. 17d and 17f). In this second mineralizing stage, the content of sulfides increases up to 2 volume percent. The latest hydrothermal Stage C, represented by the acid-sulfate alteration, includes the largest variety of sulfides in the deposits, including chalcopyrite, bornite, pyrite, lamellar covellite and chalcocite, enargite, sphalerite, galena, and tennantite (Fig. 18). These late assemblages formed as new veins and also reopened older veins. This overprinting of hydrothermal events is reflected in the copper grade. Copper grades in areas of potassic alteration with weak overprinting by younger events are normally lower than 0.3 weight percent. In areas with strong quartz-sericitic alteration, copper grades vary between 0.4 and 0.6 weight percent. Locally, where Stage C veins cut previous mineralization, the hypogene copper grades are 1 weight percent or higher.

Within the propylitic alteration zone, pyrite is the most common sulfide, but there are local, small volumes of pyrite-chalcopyrite in veins. Copper grades are normally

lower than 0.1 weight percent. In the potassic alteration zone, sulfide minerals are mainly chalcopyrite and bornite; however, the volume percentage of Cu-Fe sulfides and Fe oxide minerals vary depending on the dominant alteration mineral assemblage of the potassic alteration. For instance, andesite with pervasive biotite alteration contains up to 2 volume percent magnetite grains. Individual crystals of magnetite are small ($<60 \mu m$) and are locally replaced by bornite and chalcopyrite. The total sulfide content of biotitealtered andesite is lower than 0.5 volume percent, and the copper grade is lower than 0.2 weight percent. The content of magnetite decreases with increased presence of Kfeldspar-bearing veins. Within the intrusive rock or in the andesitic host rock, where the predominant potassic alteration assemblage is K-feldspar-quartz±biotite±anhydrite, the sulfides constitute less than 0.5 volume percent, and comprise 90 volume percent chalcopyrite and <10 volume percent bornite, with grain size ranging between 20 and 600 μ m in diameter. Bornite grains are normally smaller than 100 μ m. Copper grades vary from <0.1 to 0.3 weight percent in rock affected by K-feldspar-quartz alteration (Table 2). Within the volume of rock affected by chlorite-sericite±quartz and quartz-sericite veins of the second hydrothermal stage, the average total sulfide content increases up to 2 volume percent. The dominant sulfide is chalcopyrite with minor amounts of pyrite and molybdenite. The chalcopyrite-to-pyrite ratio is around 3:1. Where this second hydrothermal stage is strong, the hypogene copper grades vary between 0.4 and 0.6 weight percent. Chlorite-sericite±quartz veins in andesite contain up to 20 volume percent of sulfides within the thin vein filling and less than 2 volume percent in the

diameter; in the alteration halos the sulfide crystals are normally smaller than 30 μ m in

alteration halo. The vein filling contains grains of sulfides between 50 and 500 μ m in

diameter (Fig. 17d). Within the Escondida stock, in quartz of the quartz-sericitic veins, sulfides occur in cracks with thickness $<20 \ \mu$ m, between grain margins, or as disseminated sulfide grains up to 900 μ m in diameter within quartz crystals. The content of sulfides increases up to 10 volume percent within the pale-green intense alteration halos of the quartz-sericite alteration, with sulfide grains that vary between 50 and 600 μ m in diameter. Outward, beyond the area of the intense alteration halos, where the porphyritic texture of the host rock is preserved, the sulfides decrease to less than 2 volume percent of the rock and are between 30 and 100 μ m diameter. Late quartz-sericite veins with dominantly white sericite and pyrite occur mainly in the center of the deposit along the main fault zones. Where these veins are present, the total content of sulfides increases to 5 volume percent, and the hypogene copper grade is not affected. The vein filling of these pyrite-white-sericite veins with diameters up to 3 mm.

The youngest hypogene sulfides were deposited during the acid-sulfate event that represents the third and latest hydrothermal stage. Veins of the acid-sulfate event are sulfide-rich with banded textures that in some cases include minerals of the complete paragenetic evolution of this stage. After the deposition of early euhedral and banded quartz, pyrite-enargite precipitated followed by the pyrite-bornite-chalcopyrite mineral association. Later, these veins were reopened and pyrite, enargite and sphalerite with exsolved tennantite replaced the earlier bornite-pyrite-chalcopyrite. Then these late veins were reopened and fragments of the earlier sulfides were cemented by covellite and minor amounts of chalcocite that are cut and surrounded by enargite. Until this point, sulfides of the late veins were deposited with sericite and pyrophyllite and in the absence of alunite. The additional reopening of these veins allowed deposition of more pyrite with small amounts of galena and alunite. In some veins a final reopening took place that resulted in breccias cemented by alunite-pyrite, which in some cases broke all previous sulfide bands or in other cases only the central part of the vein. Not every vein of the acid-sulfate hydrothermal event includes the complete paragenetic assemblage described above, but they always include pyrite. Beyond the vein walls, fine-grained disseminated pyrite occurs within pervasive acid-sulfate alteration. Where veins of this system cut previous veins, the copper grade is normally from 0.6 to higher than 1 weight percent; pyrite-to-chalcopyrite ratios are higher than 5:1.

The characteristic overprint of several hypogene mineralizing stages resulted in large volumes of the deposit with 2 volume percent sulfides or more and with hypogene copper grades in excess of 0.5 weight percent. To date no evidence for a potassic core containing high copper grade has been found. In fact, widely spaced deep drilling below high-grade mineralization encountered potassic alteration with sporadic and weak overprinting of later alteration stages (Fig. 12). Copper grades in this deep potassic-altered zone drop to 0.2 weight percent, which is similar to the content of remnants of rock affected only by potassic alteration at high levels in the deposit. Low fracture intensity (0.2 cm⁻¹) characterizes this deep zone of potassic-altered rock in contrast to the high fracture intensity (1.0 cm⁻¹) of the upper zone, which is cut by stages B and C. In addition, study of polished sections shows that the content of Cu-Fe sulfides increases to values higher than 0.5 volume percent only where the chlorite-sericite and green-sericite mineral associations appear in vein selvages or where sulfide minerals from the advanced

argillic event are present in the veins. In contrast, pyrite is the principal sulfide added during the development of the white-sericitic event of Stage B.

Crosscutting relationships, sulfide volume percentages, and copper grades from the known part of the hypogene system of the Escondida deposit suggest that hypogene copper grades were upgraded with the development of each hydrothermal stage. Since evidence of a potassic core with high copper grade has not been observed, it is assumed that a copper grade of 0.2 weight percent or lower represents the grade produced by hydrothermal Stage A. Higher hypogene copper grades (0.6 wt %) occur only where the early orthoclase-biotite-altered rocks are overprinted by fracture-localized mineralization of younger stages. The copper deposited with the chlorite-sericite, quartz-sericite, and advance argillic events may represent an introduction of metal into the system during the development of these hydrothermal events or, perhaps, the copper was remobilized from the early low-grade K-feldspar-quartz±biotite±anhydrite assemblage. These two possibilities will be discussed further in the context of stable isotope data.

Sulfide Enrichment Blanket. Supergene sulfide ore of the enrichment blanket represents 65 weight percent of the measured total current copper resources at Escondida. The upper boundary of the supergene sulfides with the oxidized capping is subhorizontal and is vertically offset in several places across fault zones. The lower boundary is irregular, resulting in differences in the thickness of this blanket, which varies between a few meters and 400 m (Figs. 12 and 13).

Sulfides occur as disseminations and in veins and include fine-grained chalcocite, covellite, and minor amounts of digenite and idaite replacing grains of pyrite, chalcopyrite, and bornite (Alpers and Brimhall, 1989; this study). Chalcocite occurs

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across the entire thickness of this blanket, but covellite and digenite appear in the middle part and increase in content toward the bottom of this zone (Alpers and Brimhall, 1989). Copper grades typically range from 0.3 weight percent to greater than 2 weight percent, exceeding 3.5 weight percent. The best copper grades occur in the thickest parts of the supergene enrichment blanket, which corresponds with the highest intensity of fracturing. Therefore, the best supergene copper grades overlap the best hypogene copper grades in areas where strong quartz-sericite and advanced argillic events overprint early potassic alteration.

Leached Capping Zone. The upper limit of the leached capping zone is marked by the modern land surface, whereas its lower limit varies from a few meters below the surface, above the zone of copper oxides, to more than 200 m below the surface, over the enrichment blanket (Figs. 12 and 13). Copper and molybdenum grades vary from <100 to 600 ppm and from less than 10 to 480 ppm, respectively (Ortiz et al., 1996). The limonite compositions of this zone exhibit good spatial correlation with supergene grades and thickness (Alpers and Brimhall, 1989). The higher grade and thicker zones of the underlying supergene Cu-sulfide blanket normally lie below hematite, whereas thinner zones with lower supergene copper grades lie below jarosite-rich capping. Goethite is most abundant in the western part of the deposit, where copper oxides are dominant.

Copper Oxides. The term copper oxide is used to group non-sulfide copper minerals including oxides, silicates, sulfates, and carbonates. This type of mineralization represents 16 weight percent of the total copper resource at Escondida. The most common minerals are brochantite, antlerite, atacamite, chrysocolla, copper wad, and tenorite. They are present mainly along fractures hosted by andesite with biotite and

chlorite-sericite alteration. This ore type also is found in the Escondida stock where K-feldspar alteration is preserved, but it is volumetrically less important that in the biotiteor chlorite-sericite-altered andesite. Copper grades vary from less than 0.2 to 1.5 weight percent, and the thickness of mineralized rock ranges from a few meters to 200 m.

CHAPTER 4

GEOCHRONOLOGY

Isotopic ages of igneous rocks from the Escondida district have been presented by Marinovic et al. (1992), Richards et al. (2000), and Richards and Boyce (2001). K-Ar ages of alteration minerals from the Escondida deposit were published by Alpers and Brimhall (1988) and by Ojeda (1990). The present work further constrains the time evolution at the deposit scale, including crystallization ages of four different intrusive rocks from the deposit (U-Pb ages on zircons), ages of the hydrothermal minerals $({}^{40}\text{Ar}/{}^{39}\text{Ar}$ ages on biotite, sericite, and alunite), and a Re/Os age on molybdenite.

Escondida District and Regional Geochronology

Isotopic ages of igneous rocks and alteration minerals from the Escondida region and district range from 280 to 31 Ma (Fig. 19 and Table 5). The older ages mark the development of voluminous felsic magmatism at the end of the Paleozoic, which is characteristic of northern Chile. The Jurassic ages of andesite intruded and covered by late Paleozoic rhyolites are interpreted as Paleozoic ages disturbed by a Jurassic metamorphic event (Fig. 19). The gabbros reported by Marinovic et al. (1992) and by Richards et al. (2000) yield isotopic ages (K-Ar and Ar-Ar) of 70 and 75 Ma (Fig. 20).

At Escondida there were two Cenozoic periods of magmatism separated by a hiatus of 5 million years. The andesite-rhyolite volcanic rocks of the Augusta Victoria Formation, host rock of the Escondida deposit, were deposited between 60 and 50 M (K-Ar ages; Fig. 20). After a period of magmatic quiescence, the first dioritic plutons



Fig. 19: A compilation of published ages from the Escondida region. Shown are the two main magmatic periods: 1) Late Paleozoic felsic magmatism associated with the western margin of Gondwana and; 2) Late Cretaceous-middle Tertiary Andean magmaticevent. Diamonds are K-Ar ages, crosses are Ar-Ar ages, and squares represent U-Pb ages.



Fig. 20: A closer view of the distribution of ages associated with the Andean magmatic cycle in the Escondida region. Three magmatic periods are separated: a 70-75 Ma period represented by a few outcrops of grabbros in the southern edge of the district; a 50-60 Ma event that includes andesite and rhyolite volcanic rocks of the Augusta Victoria Formation (host rock of the Escondida stock); and the 45-34 Ma magmatic event that includes the diorites, productive granodiorites, and late rhyodacitic intrusive and volcanic rocks of the district. Circles and vertical bars represent K-Ar ages and their 2σ errors, crosses are Ar-Ar ages, and squares represent U-Pb ages.

were intruded in the western edge of the district (Figs. 4 and 5). The emplacement of dioritic intrusive rocks lasted approximately 11 Ma (45 to 34 Ma, Fig. 20). Isotopic ages from the granodiorites that are associated with the mineralization of the district vary between 39 and 36 Ma (Fig. 20), and ages from postmineral rhyolite and dacite intrusive rocks range from 38 Ma to 31 Ma (Fig. 20).

Richards et al. (2000) suggest that the ore-forming magmatism in the Escondida district took place in a short period of intense magmatic activity at approximately 38 Ma (U-Pb). They also argue that such an intense, focused magmatism was essential for the development of the large porphyry copper systems in the district. More detailed discussion on the time evolution of the Late Eocene-Early Oligocene intrusive rocks and the development of the mineralization in the Escondida deposit is presented below in this chapter and in Chapter 6 of this study.

Escondida Deposit Geochronology

Introduction

Alpers and Brimhall (1988) and Ojeda (1990) were the first to publish ages of the hydrothermal events of the Escondida deposit. Their study used K-Ar analyses to bracket the evolution of the hydrothermal system between 39 and 31 Ma (Fig. 28). However, they neglected ages older than 35 Ma, arguing possible inheritance from the andesitic host rock or contamination induced by excess ⁴⁰Ar in alunite.

Zentilli et al. (1994) reported a U-Pb age on zircons of 32.6 ± 2 Ma from a composite sample of rhyolitic rocks from the Escondida deposit and from a location close to, but outside of, the mineralized area. This is a discordant lower intercept date with an upper intercept indicating Paleozoic inheritance. Richards et al. (2000) indicate that if

the zircon population from outside the mineralized zone is removed from the calculation and if 2_{σ} error is used in the statistical calculation, the discordant lower intercept moves to 34.9 ± 0.4 Ma. However, they also pointed out that the significance of the error is meaningless since the regression line includes only two points. Richards at al. (2000) added a new discordant U-Pb date for Cerro-Sureste rhyolite, which yields a lower intercept at 33.6 ± 2.3 Ma and upper intercept in the Late Paleozoic.

Richards et al. (2000) interpreted that the maximum age of the hydrothermal alteration must be that of the crystallization age of the associated porphyritic rocks. They pursued this argument by dating a sample from the Colorado Grande intrusive phase, which also resulted in a discordant age with a lower intercept at 37.9 ± 1.1 Ma and an upper intercept indicating Paleozoic inheritance. In the calculation of the lower intercept for the sample from the Cerro-Sureste rhyolite and the Colorado Grande intrusive phase, Richards et al. (2000) included an upper value of ~288 Ma, which was an age with weak concordance obtained from a sample of the Paleozoic basement of the district (Zal3 in Table 5). With the addition of this Paleozoic point to the calculation, they proposed that it would be possible to convert an imprecise date to a precise date. It is important to note that the addition of the Paleozoic point to the calculations would work only if the late Eocene-Oligocene granodioritic rocks inherited, exclusively, ~288 Ma old zircons. Otherwise, the calculated ages may include a much larger error than that of the ages reported by Richards et al. (2000).

Sample	Area	Rx type	Alteration	Age	Error	Method	Material	Preparation	Ву	Location	N-S	E-W
				Ма	Ма							
Zal-2Rch	Zaldivar	Rhyolite	Unknown	290	4	U-Pb	Zircon	Separate	Richards	Open Pit,	7322200	493700
Zal-3Rch	Zaldivar	Rhyolite	Sericitic	290	4	U-Pb	Zircon	Separate	Richards	Open Pit	7322200	493900
Zal-1Rch	Zaldivar	Granodiorite	Sericitic	38.7	1.3	U-Pb	Zircon	Separate	Richards	Undergound	7315800	493700
Zal-1Rch	Zaldivar	Granodiorite	Sericitic	37.4	0.18	Ar/Ar	Biotite	Separate	Richards	unknown loc.	7315800	493700
IM-154	Chimborazo	Granodiorite	Fresh	38.09	0.3	Ar/Ar	Biotite	Separate	Richards	Roadcut	7329000	485800
IM-47	Regional	Hb-Diorite	Unknown	38.3	0.23	Ar/Ar	Hornblende	Separate	Richards	Outcrop	7322768	505397
IM-70	Regional	Hb-Diorite	Unknown	37.2	0.17	Ar/Ar	Hornblende	Separate	Richards	Outcrop	7327012	505032
IM-79	Regional	Andesite	Unknown	37.38	0.19	Ar/Ar	Hornblende	Separate	Richards	Outcrop	7319665	504211
IM-86	Regional	Dacite	Unknown	265.8	1.04	Ar/Ar	Hornblende	Separate	Richards	Outcrop	7331395	499788
IM-90	Regional	Dacite	Unknown	34.89	0.41	Ar/Ar	Hornblende	Separate	Richards	Outcrop	7322080	496395
IM-110	Regional	Hb-Diorite	Unknown	36.94	0.42	Ar/Ar	Hornblende	Separate	Richards	Outcrop	7332057	491953
IM-159	Regional	Hb-Gabbro	Unknown	75.71	0.54	Ar/Ar	Hornblende	Separate	Richards	DDH-149-270m	7315600	492900
IM-158	Regional	Hb-Gabbro	Unknown	77	0.29	Ar/Ar	Hornblende	Separate	Richards	Outcrop	7308994	487400
Esc2	Escondida	Granodiorite	Weak sericitic	35.9	0.3	Ar/Ar	Biotite	Separate	This Study	DDH1343-300m	15800	108225
Esc5	Escondida	Rhyolite	Weak sericitic	33.6	0.7	Ar/Ar	Biotite	Separate	This Study	Open Pit, Co. SE	15800	108700
Esc1	Escondida	Granodiorite	Weak sericitic	35.8	0.2	Ar/Ar	Biotite	Separate	This Study	D258-891	15900	107400
Esc7	Escondida	Andesite	Biotization	37.5	0.6	Ar/Ar	Biotite	Separate	This Study	DHH353-97m	15450	107478
Esc8	Escondida	Vein/Perv	Weak chloritic	34.8	0.4	Ar/Ar	Biotite	Separate	This Study	DDH17-350m	16068	107637
Esc9	Escondida	Vein	Weak chloritic	36.2	0.4	Ar/Ar	Biotite	Separate	This Study	DDH17-210m	16068	107637
Esc24	Escondida	Polymet-vein	Adv-Arg	49.9	0.3	Ar/Ar	Illite	Separate	This Study	Open pit	14803	108798
Esc14	Escondida	Alteration	Sericitic	35.9	0.2	Ar/Ar	Sericite	Separate	This Study	Open pit	16580	107650
Esc15	Escondida	Alteration	Sericitic	40.7	0.2	Ar/Ar	Sericite	Separate	This Study	D1463-120	16451	107478
Esc19	Escondida	Alteration	Sericitic	40.7	0.2	Ar/Ar	Sericite	Separate	This Study	D1452-300m	15611	107645
Esc20	Escondida	Alteration	Sericitic	39.98	0.21	Ar/Ar	Sericite	Separate	This Study	D1440-300m	16461	108635
Esc28	Escondida	Alteration	Adv-Arg	35.7	0.3	Ar/Ar	Alunite2	Separate	This Study	Co. Grande	15770	108132
Esc29	Escondida	Alteration	Adv-Arg	35.9	0.3	Ar/Ar	Alunite1	Separate	This Study	Co Chico	16450	108600
Esc1	Escondida	Granodiorite	Weak sericitic	37.2	0.8	U-Pb	Zircon	Separate	This Study	DDH71-484m	15746	108177
Esc2	Escondida	Granodiorite	Weak sericitic	37.7	0.8	U-Pb	Zircon	Separate	This Study	DDH1343-300m	15800	108225
Esc4	Escondida	Rhyolite	Adv-Arg	39	1.5	U-Pb	Zircon	Separate	This Study	RD-937-250m	16450	108600
Esc6	Escondida	Rhyodacite	Argillic	35.6	1.2	U-Pb	Zircon	Separate	This Study	East Wall	17100	107000
Esc31	Escondida	Vein	Adv-Arg	33.7	0.3	Re-Os	Molybdenite	Separate	This Study	East Wall	17000	107600
ESC1-Rch	Escondida	Granodiorite	Kfds-Bt-Ser	37.9	1.3	U-Pb	Zircon	Separate	Richards	Drill hole	unknown	unknown

 Table 5. Ages from the Escondida Region.

Samples from this study in bold, all in local mine coordinates. All other samples in UTM coordinates. Abbreviations in Appendix F.

Table 5. Continued

Sample	Area	Rx type	Alteration	Age	Error	Method	Material	Preparation	Ву	Location	N-S	E-W
				Ма	Ма							
ESC4-Rch	Escondida	Rhyolite	Sericite	34.7	1.7	U-Pb	Zircon	Separate	Zentille	East Wall	unknown	unknown
Ojeda	Escondida	Andesite	Biotite	39.1	2.2	K-Ar	Biotite	Unknown	Ojeda	DDH-258-891m	7315950	493450
CAKAR-10	Escondida	Alteration	Adv-Arg	38.3	3	K-Ar	Alunite	Separate	Alpers	DDH-47-336m	7317200	492968
CAKAR-18	Escondida	Alteration	Adv-Arg	35.7	2.8	K-Ar	Alunite	Separate	Alpers	Trench 38	7317035	492360
ESAD-2	Escondida	Andesite	Biotite-Chlorite	35.4	3.6	K-Ar	Whole Rx	Whole Rock	Alpers	DDH13-m?	7318000	491609
Ojeda	Escondida	Andesite	Unknown	34.6	3.6	K-Ar	Whole Rx	Whole Rock	Ojeda	Unknown loc.		
CAZ-321	Escondida	Rhyolite	Pyrophyllite-Ser	33.7	2.8	K-Ar	Sericite	Concentrate	Alpers	Trench 38	7314410	494580
ESAD-1	Escondida	Breccia	Biotite	33.7	2.6	K-Ar	Biotite	Separate	Alpers	DDH-17-346.5m	7318050	492012
Ojeda	Escondida	Granodiorite	Unknown	33.6	3.4	K-Ar	Whole Rx	Whole Rock	Ojeda	Unknown loc.		
CAKAR-13	Escondida	Andesite	Biotite-Chlorite	33.2	2.8	K-Ar	Biotite	Concentrate	Alpers	DDH-149-270m	7315600	492900
CAKAR-14	Escondida	Andesite	Bt-Chl-Ser	32.8	2.6	K-Ar	Biotite	Separate	Alpers	DDH-32-446m	7315800	492800
Ojeda	Escondida	Granodiorite	Biotite	31.9	2.4	K-Ar	Biotite	Unknown	Ojeda	Unknown loc.		
Ojeda	Escondida	Granodiorite	Unknown	31.8	2.4	K-Ar	Whole Rx	Whole Rock	Ojeda	Unknown loc.	7315950	493450
CAZ-241	Escondida	Rhyolite	Adv-Arg	31.6	3.2	K-Ar	Sericite	Concentrate	Alpers	Roadcut	7315300	494190
CAKAR-11	Escondida	Rhyodacite	Sericite-Chlorite	31.5	2.8	K-Ar	Sericite	Separate	Alpers	DDH-165-336m	7315800	493500
CAKAR-12	Escondida	Rhyodacite	Sericite	31	2.8	K-Ar	Whole Rx	Whole Rock	Ojeda	DDH-161-451m	7315800	493400
Serna1	Regional	Andesite	Unknown	55	1.4	K-Ar	Biotite	unknown	SERNAGEOMIN	Outcrop	7343277	486161
Serna2	Regional	Andesite	Unknown	42.1	1.5	K-Ar	Whole Rx	Whole Rock	SERNAGEOMIN	Outcrop	7335245	465031
Serna3	Regional	Diorite	Unknown	42	4.5	K-Ar	Biotite	Unknown	SERNAGEOMIN	Outcrop	7333936	481287
Serna4	Regional	Diorite	Unknown	43.9	1.3	K-Ar	Biotite	Unknown	SERNAGEOMIN	Outcrop	7328386	478185
Serna5	Regional	Latite	Greenshist	169	6	K-Ar	Whole Rx	Whole Rock	SERNAGEOMIN	Outcrop	7327286	498005
Serna6	Regional	Tonalite	Greenshist	196	6	K-Ar	Whole Rx	Whole Rock	SERNAGEOMIN	Outcrop	7324268	499351
Serna7	Regional	Andesite	Unknown	34.6	3.1	K-Ar	Whole Rx	Whole Rock	SERNAGEOMIN	Outcrop	7308305	494903
Serna8	Regional	Andesite	Unknown	59.1	1	K-Ar	Biotite	Unknown	SERNAGEOMIN	Outcrop	7308306	494904
Serna9	Regional	Diorite	Unknown	48.9	1.5	K-Ar	Biotite	Unknown	SERNAGEOMIN	Outcrop	7306758	460822
Serna10	Regional	Diorite	Unknown	77	2	K-Ar	Biotite	Unknown	SERNAGEOMIN	Outcrop	7292558	482293
Serna11	Regional	Diorite	Unknown	41	1.8	K-Ar	Biotite	Unknown	SERNAGEOMIN	Outcrop	7291817	488060
Serna12	Regional	Tonalite	Unknown	192	6	K-Ar	Whole Rx	Unknown	SERNAGEOMIN	Outcrop	7293936	491758
Serna13	Regional	Tonalite	Unknown	239	9	K-Ar	Biotite	Unknown	SERNAGEOMIN	Outcrop	7299543	476736
Serna14	Regional	Tonalite	Unknown	265	10	K-Ar	Hornblende	Unknown	SERNAGEOMIN	Outcrop	7298961	476789
Serna15	Regional	Andesite	Unknown	56.9	1.6	K-Ar	Hornblende	Unknown	SERNAGEOMIN	Outcrop	7340185	460683

All samples from this page in UTM coordinates. Abbreviations in Appendix F.

The present work further constrains the age of the hydrothermal evolution by adding $14 \ {}^{40}\text{Ar}/{}^{39}\text{Ar}$ ages for hydrothermal biotite, sericite, and alunite. Four additional concordant U-Pb ages were obtained for four different intrusive phases, and one age for mineralization was obtained from Re-Os analysis on a molybdenite sample (Table 5).

U-Pb Ages

Several zircon fractions were analyzed from the first two intrusive phases of the Escondida stock, the rhyolitic dome that cut the Escondida stock, and a late barren dike that intruded the Cerro-Sureste rhyolite and postdates all mineralization in the deposit (Figs. 21 to 24). The U-Pb systematics of dating are described by Faure (1986), and the laboratory methodology is presented by Gehrels and Boghossian (2000). The results of the U-Pb analysis are listed in Table 5 and are depicted in figures 21 to 24.

The U-Pb results show that all samples have Paleozoic inheritance. The analyzed zircon sizes vary between 100 and 250 microns (Appendix D), and most of them were abraded in an air-abrasion device before analysis. All four samples yielded concordant ages that range from ~38 to ~34 Ma. Seven zircon grains were analyzed from sample "Esc1Zr" of the Colorado Grande intrusive phase. From these seven grains, five gave concordant ages, setting the crystallization age of this intrusive phase at 37.2 ± 0.8 (Table 5, Fig. 21). All errors represent two times the standard deviation. Five out of six zircon grains analyzed from sample "Esc2Zr" of the Escondida intrusive phase yielded concordant ages that overlapped, giving a crystallization age for this intrusive phase of 37.7 ± 0.8 (Fig. 22).



Fig. 21. U-Pb zircon data from sample Esc1Zr of the Colorado Grande intrusive phase. a) All zircon data with an upper intercept age of 293 ± 23 Ma and a lower intercept close to 38 Ma. b) A close-up view of the lower intercept showing concordant zircon data with an age of 37.2 ± 0.8 Ma, with error defined at 2s.



Fig. 22: U-Pb zircon data from sample Esc2Zr of the Escondida intrusive phase. a) All zircon data with an upper intercept age of 634 ± 211 Ma and a lower intercept close to 38 Ma. b) A close-up view of the lower intercept showing concordant zircon data with an age of 37.7 ± 0.8 Ma, with error defined at 2s.



Fig. 23: U-Pb zircon data from sample Esc4Zr of the rhyolite dome. a) All zircon data with an upper intercept age of 477 ± 155 Ma and a lower intercept close to 38 Ma. b) A close-up view of the lower intercept showing concordant zircon data with an age of 39.5 ± 1.5 Ma, with error defined at 2s.



Fig. 24: U-Pb zircon data from sample Esc6Zr of a late barren rhyodacitic dike. a) All zircon data with an upper intercept age of 307 ± 37 Ma and a lower intercept close to 35 Ma. b) A close-up view of the lower intercept showing concordant zircon data with an age of 35.6 ± 1.2 Ma with error defined at 2s.

Nine zircon grains from sample "Esc4Zr" of the rhyolitic dome were analyzed and yielded varying ages. Four of these ages presented Paleozoic inheritance and therefore gave discordant ages (Fig. 23). Four zircon grains gave concordant ages with the largest U-Pb error bar of all the four samples analyzed in this study. The crystallization age of the rhyolitic dome is set at 39 ± 1.5 Ma (Fig. 23). However, its porphyry-style mineralization and the fact that the rhyolitic dome cuts the Escondida granodioritic stock suggest a maximum age of crystallization at the lower limit of the U-Pb analysis, at approximately 37.5 Ma (Figs. 23 and 28).

Only one zircon grain from the sample "Esc6Zr" (late barren dike) yielded a discordant age, and the other five analyzed zircon grains gave concordant ages that overlap, setting the age of crystallization for this post-mineralization intrusive rock at 35.6 ± 1.2 Ma (Fig. 24). Since field observations indicate that this rock postdates all the mineralization of the other intrusive events, its crystallization age sets the youngest age limit of the hydrothermal activity and magmatism at the Escondida deposit (Fig. 28). ⁴⁰Ar/³⁹Ar Ages

A total of 13 samples from the Escondida deposit were dated using the ⁴⁰Ar/³⁹Ar method at the University of Nevada, Las Vegas, Isotope Geochronology Laboratory. A summary of the lab report is presented in this chapter, and the complete report is included in Appendix C. These samples include biotite, sericite, illite, and alunite (Table 5). Biotite samples include igneous biotite crystals from the Colorado Grande (Esc1Bt) and the Escondida (Esc2Bt) intrusive phases of the Escondida Stock; biotite from the Cerro-Sureste rhyolite (Esc5Bt); biotite from andesite with pervasive biotitic alteration (Esc7Bt); and biotites from hydrothermal veins (Esc8Bt and Esc9Bt; Table 5). Sericite samples were separated from two dark-sericite-dominated and two white-sericitedominated samples. Two samples of alunite were separated from vein samples that cut the rhyolitic dome, and one sample of illite was also separated from one of these samples. The 40 Ar/ 39 Ar systematics of dating is presented in Appendix C. The results of 40 Ar/ 39 Ar analysis are listed in Table 5 and are depicted in figures 25, 26, and 27.

Biotite

Igneous Biotite.

Igneous Biotite from Phase 1 and Phase 2 of the Escondida Stock. Books of igneous biotite (>1mm in diameter) were hand picked from the Colorado Grande (Esc1Bt) and the Escondida (Esc2Bt) granodioritic intrusive phases that are interpreted to be associated with the development of the Escondida porphyry copper deposit. Microscopic analysis revealed the presence of chlorite in thin layers within the biotite crystals. The results of microprobe analysis plotted in the F/OH versus Mg/Fe ratios diagram suggest that these books of igneous biotite have experienced hydrothermal alteration (Fig. 15); therefore, their ages may also indicate hydrothermal reheating. Both samples yield Ar-Ar ages close to 36 Ma, which are at least one million years younger than the crystallization ages of the igneous rocks given by U-Pb analysis and may corroborate a younger reheating of the system (Table 5; Fig. 27). The ⁴⁰Ar/³⁹Ar data from samples "Esc1Bt" and "Esc2Bt" are presented in Table 5 and plotted in figures 25 to 26.

The Ar-Ar analysis of sample "Esc1Bt" gave a nearly ideal flat age spectrum with most ages close to 36 Ma, except for older ages in the initial 2 percent of gas released (Fig. 26). The isochron age of 35.8 ± 0.4 Ma is the best estimate of the age of the Esc1Bt sample (Fig. 25).

Data from sample "Esc2Bt" also show an almost flat age spectrum, with ages of close to 36 Ma, with the exception of a few discordant ages in the first 5 percent of gas released (Fig. 26). The total gas age of 36.4 ± 0.4 Ma is almost identical to the ages of the nearly flat age segment (Fig. 26).

Igneous Biotite from Cerro-Sureste Rhyolite ("Esc5Bt" Sample). Books of igneous biotite were handpicked from a sample of the Cerro-Sureste rhyolite (Esc5Bt) that cuts the Escondida stock and cuts potassic and quartz-sericitic alteration. The Cerro-Sureste rhyolite is cut by veins with the advanced argillic mineral association. Microscopic analysis revealed the presence of chlorite in thin layers within the biotite crystals. The results of microprobe analysis plotted in the F/OH versus Mg/Fe ratios diagram suggest that these books of igneous biotite have experienced hydrothermal alteration (Fig. 15); therefore, their ages may also indicate hydrothermal reheating. The ⁴⁰Ar/³⁶Ar data from sample "Esc5Bt" is presented in Table 5 and plotted in figures 25 and 26.

The data from sample "Esc5Bt" does not produce an obvious plateau age (Fig. 26). A total gas age of 36.2 ± 0.4 Ma and a valid isochron of 33.6 ± 1.4 Ma are calculated (Fig. 26). The best estimate of the age of this sample is the isochron age.

Hydrothermal Biotite. Three samples of hydrothermal biotite were separated for incremental laser heating. Sample "Esc9Bt" was separated from an orthoclase-biotite-anhydrite vein where crystals of biotite were larger than 1 mm, but all crystals showed chloritic alteration. The sample that was run by laser incremental heating was separated by a combination of handpicking and magnetic separation. Microprobe analysis indicates

that the final sample contained intergrowths of chlorite within biotite. Despite the common presence of chlorite impurities, this sample was analyzed.

Sample "Esc9Bt" reveals a slightly discordant segment with ages close to 38 Ma. No plateau age is defined for this age spectrum and a total gas age of 36.0 ± 0.4 Ma is calculated (Fig. 27). The data from steps 5 to 12, including close to 46 percent of the gas released, define a non-statistically valid isochron with an age of 39.8 ± 0.6 . The best estimate of the age of this sample is the total gas age (Fig. 27).

Sample "Esc8Bt" is from an andesite that was collected at the contact with the Escondida intrusive phase (Table 5). This sample presents strong, pervasive fine-grained biotization that is cut by a thin vein of biotite. All biotite grains are smaller than 1 mm, and magnetic separation was used to isolate the final sample. As in sample "Esc9Bt", chlorite impurities were observed during microprobe analysis, but chloritization is less intense. The Ar-Ar data from this pervasive biotite gave an age spectrum with almost concordant ages close to 35 Ma for most of the gas released and a total gas age of 34.8 ± 0.4 Ma. No plateau age was defined for this age spectrum. Data between steps 4-16, comprising almost 98 percent of the gas released, define a valid isochron, with an age of 34.8 ± 0.8 Ma. The best estimate of the age of this sample is the isochron age.

Sample "Esc7Bt" is from an andesite with pervasive fine-grained biotitic alteration with crystals smaller than 1mm; therefore, their separation was carried out using the magnetic susceptibility of biotite. Of all the hydrothermal biotites run for ⁴⁰Ar/³⁹Ar dating, this sample exhibits the least chloritization. The age spectrum for sample "Esc7Bt" gave anomalously old ages for the first 15 percent of gas released, followed by a slightly discordant segment with ages of close to 39 Ma for the remaining gas released. The calculated total gas age was 43.7 ± 0.4 Ma. There was no plateau defined. The data from steps 4 to12, comprising close to 62 percent of the gas released, defined a valid isochron with an age of 37.5 ± 0.6 . The best estimate of the age of this sample is the isochron age (Fig. 25).

Sericite

Sericite is a very abundant hydrothermal mineral in the Escondida deposit, but crystals are always smaller than 25 microns. Sericite occurs in part with the late hydrothermal stage of the porphyry copper system that predates the emplacement of rhyolite and is also associated with minerals associated with the advanced argillic hydrothermal event that cuts the rhyolites. Samples of sericite and illite with grain sizes smaller than 40 microns were separated by crushing, sieving, wet separation by hand decanting of fine material, and finally the fraction <40 microns was centrifuge separated. The samples analyzed were selected after X-ray studies. These samples showed good sericite patterns, probably with small amounts of kaolinite and pyrophyllite.

None of the sericite samples run for ⁴⁰Ar/³⁹Ar dating yielded a plateau or a statistically valid isochron with calculated gas ages ranging from 40 to 36 Ma, suggesting problems with the quality of the samples. The lab report included in Appendix B indicates that the quality of samples may be affected by the mixing of grains from different events, reheating, or by the susceptibility of the sample to the effects of reactor-induced loss of ³⁹Ar (recoil) due to the small grain sizes. Age spectrum patterns like the one of sample "DarkSer2" presented in Figure 27 and discussed in Appendix C are similar to those patterns of white micas from Naxos, Greece, reported by Wijbrans and McDougall (1986). Wijbrans and McDougall interpreted the patterns found in the Greek

samples to contain two generations of white micas, with the resulting spectrum being a combination of the two—one older and one younger. This mixing of grains also could have been possible for the sericite samples from Escondida. The 40 Ar/ 39 Ar dates from sericites and illite may be considered as rough limits of the magmatic hydrothermal history at the Escondida deposit, but they are not used in discussions of the temporal evolution of the Escondida deposit (Fig. 27).

<u>Alunite</u>

Two alunite samples (Esc28ALU and Esc29ALU) were separated from veins that cut the rhyolitic dome. One sample comes from the Colorado Grande hill and the second one from the Colorado Chico hill (Fig. 26). These two samples of alunite are coarse grained with pinkish color, occurring as alteration selvages on veins with sulfide mineral association related to the advanced argillic event. The large-sized crystals of alunite in these veins made it easy to hand separate samples for testing. Both samples yielded robust ages close to 36 Ma. The description of the data from alunite samples described in the following paragraphs indicates that the age from sample "Esc29ALU" is more robust than the age from "Esc28ALU".

The heating steps data from sample "Esc29ALU" define a plateau segment giving a valid age of 35.2 ± 0.4 Ma. This age spectrum is confirmed by an isochron age defined



Fig. 25: Inverse isochron correlation diagrams of 40 Ar- 39 Ar dating results for biotites and alunites from igneous rocks and hydrothermal events of the Escondida deposit. The steps included in each isochron calculation and the percent of gas released is given. 2σ errors and the mean square of weighted deviates (MSWD) also are given.



<u>Fig. 26</u>: Step-heating ⁴⁰Ar–³⁹Ar age spectra of biotites and alunite from igneous rocks and hydrothermal events of the Escondida deposit. Plateau, total gas, and isochron ages are from Figure 25. 2σ errors and the initial ³⁶Ar/⁴⁰Ar were calculated from the inverse isochron correlations (Fig. 25).



Fig. 27: Step-heating 40 Ar- 39 Ar age spectra of sericites, illite, and one biotite. These samples are not included in the discussion of time evolution of the Escondida deposit because the data do not define robust ages, probably due to mixing of grains of different events and reheating of the system.

by data from steps 2 to14 (>99% of the total gas released) that yields an age of 35.7 ± 0.6 Ma. The isochron is the best estimate of the age of the sample (Fig. 25).

The sample "ALU1" gave an age spectrum of 35.4 ± 0.4 Ma. No isochron age is defined for this sample and therefore the plateau age is the best estimate of age (Fig. 26).

Re-Os Ages of Molybdenite

Ruiz and Mathur (1999) reported that pyrite and chalcopyrite samples separated from each of the different recognized hydrothermal events of the Escondida deposit failed to provide reliable information because of the high concentration of Re contained in the samples. Ruiz and Mathur (1999) suggest that these results could be a reflection of supergene alteration or a reflection of trace quantities of molybdenite. To overcome the problem of excess Re of the common sulphides one sample (Esc31Mo) of molybdenite was analyzed, yielding an age of 33.7 ± 0.3 (Table 5, Fig. 28). The molybdenite sample was separated from a vein that cuts the Escondida stock. The mineralogy of this vein includes pyrite, chalcopyrite, covellite, and molybdenite with selvages of white sericite and probably pyrophyllite plus quartz (Table 5).

The systematics of Re-Os dating has been reviewed by McCandless et al. (1993), and the analytical technique of Re-Os has been summarized by Mathur et al. (2000a).

Interpretation and Discussion

Crosscutting relationships observed in the field are the first constraints used to analyze the time of evolution of the Escondida deposit. Field data indicate that the Escondida stock is the oldest intrusive event of the deposit, and its strong spatial relationship to the pervasive biotite alteration halo suggests their coeval evolution (Fig. 11).

Pervasive biotite and biotite veins predate the emplacement of the rhyolitic rocks; therefore, the age of the rhyolite dome sets a younger limit for the temporal evolution of the early potassic alteration. Veins that include sericite are present in the granodiorite and the rhyolites; for this reason they are indicative of only relative timing. Polymetallic veins with alunite are abundant in the rhyolitic rocks, but also affect the Escondida stock; thus, we can infer that at least some of the polymetallic veins with alunite postdate the potassic event. Finally, the late barren dikes that cut all intrusive rocks of the deposit post a younger limit on the magmatic and hydrothermal activity in the Escondida deposit.

Once the field relationships among geological features were established, the isotopic ages can further constrain the geochronology of the Escondida deposit. No crosscutting relationships have been observed between the Colorado Grande and Escondida intrusive phases, but they are the first two intrusive phases within the Escondida stock. Crystallization ages of zircons from the Colorado Grande and the Escondida intrusive phases yield very similar U-Pb (Zircon) ages, 37.2 ± 0.8 and 37.8 ± 0.8 , respectively. This age range establishes the older limit of the hydrothermal alteration in the deposit. The field relationship between the pervasive biotitic alteration and the Escondida stock is supported by the 40 Ar/ 39 Ar age of sample "Esc7Bt" that yielded an age of 37.5 ± 1.2 Ma. Therefore, the main porphyry system, which includes the emplacement of the Escondida stock and the development of the early potassic and probably part of the

late quartz-sericite mineral assemblages, was developed between 37 and 38 Ma , which is within the error bars of the 40 Ar/ 39 Ar and U-Pb results.

The minimum crystallization age of emplacement of the rhyolite dome (Esc4Zr = 37.5 to 38 Ma) overlaps the maximum age of the Colorado Grande intrusive phase of the Escondida Stock. This overlap of ages indicates that the porphyry system evolved in a relatively short period of time, close to 38 Ma, as was suggested in 2000 by Richards et al. (Fig. 28).

Two robust ⁴⁰Ar/³⁹Ar ages on alunite yield 35. 7 ± 0.3 and 35.9 ± 0.3 , indicating a second hydrothermal event for the Escondida deposit (Figs. 25, 26, and 28). The alunite was separated from polymetallic veins that cut the rhyolitic dome, which sets a minimum emplacement age for the rhyolitic dome. Biotite veins are cut by the rhyolite dome; however, ⁴⁰Ar/³⁹Ar ages of biotite from hydrothermal veins and the first two igneous phases of the Escondida stock yield ages very close to ~36 Ma. These ~36 Ma ages suggest that biotite was reheated above the Ar-closure temperature of 280°C during the evolution of the younger hydrothermal event, with the consequent resetting of the isotopic clocks (Fig. 28). The Re/Os age of 33.7 ± 0.3 Ma age on a molybdenite sample documents a younger hydrothermal event close to 34 Ma (Fig. 28).

The age of emplacement of the Cerro-Sureste rhyolite cannot be unequivocally placed in a narrow time bracket. The U-Pb age of 34.7 ± 1.7 reported by Richards et al. (2000) for the emplacement of the Cerro-Sureste rhyolite extends its upper age limit to the age reported by the alunite samples (~36 Ma), which thus suggests that the emplacement of the second rhyolite and the development of the advanced argillic event were coeval. This argument would be acceptable only if the age of the hydrothermal

mineralization that cuts the Cerro-Sureste rhyolite was also 36 Ma old. However, there is no unequivocal data that support this argument, as the samples of alunite were taken from veins that cut the rhyolitic dome, and as mentioned above, no field relationship has been observed between the two rhyolites.

The mineralization that cuts the Cerro-Sureste rhyolite also may be associated with the youngest 34 Ma hydrothermal event. The 40 Ar/ 39 Ar age of weakly chloritized igneous biotite crystals from the Cerro-Sureste rhyolite yields 33.6 ± 1.4 Ma, which is similar to the Re/Os age on molybdenite. Therefore, it can be argued that the Cerro-Sureste rhyolite was emplaced sometime between 36 and 34 Ma, and its biotite ages were reset during the evolution of the youngest hydrothermal event at ~34 Ma. The lower (older) age limits of the late barren dikes that cut the Cerro-Sureste rhyolite overlap with the upper (younger) ages of the molybdenite and the biotite from the Cerro-Sureste rhyolite, suggesting a time of emplacement for these late barren dikes close to 34 Ma (Fig. 28).

In summary, between 38 and 34 Ma three separate hydrothermal events were involved in the evolution of the Escondida deposit. The oldest event is associated with the emplacement of the Escondida stock and the development of the main porphyry copper system, close to 38 Ma. Closely following the development of the porphyry copper system, a rhyolite dome intruded the Escondida stock. The overlap of the lower age limit of the rhyolite dome with the crystallization ages of the Escondida stock and hydrothermal biotite argues for an evolution of the magmatic-hydrothermal system in a relatively short period of time. This is in agreement with thermal models that proposed cooling histories for shallowly emplaced magmas on the order of thousands or a few hundreds of years (Cathles et al., 1977; Norton, 1982). An epithermal high-sulfidation event overprinted the early mineralization and igneous rocks at approximately 36 Ma, and finally a younger advanced-argillic mineralizing pulse affected previous hydrothermal and magmatic events at approximately 34 Ma. The Cerro-Sureste rhyolite was emplaced sometime between 36 and 34 Ma, with biotite ages reset during the evolution of the youngest hydrothermal event at 34 Ma. Immediately after the development of the last hydrothermal activity at an inferred age of about 34 Ma, the late barren rhyodacitic dikes were emplaced, marking the end of the magmatic-hydrothermal evolution in the Escondida deposit (Fig 28).



Fig. 28: Schematic representation of the temporal evolution of the magmatic-hydrothermal events that formed the Escondida deposit. The diagram includes only ages considered robust from the analysis presented in the text. Squares represent U-Pb ages of crystallization of intrusive rocks, diamonds and circles are Ar-Ar ages on biotite and alunite, respectively, and triangles are Re-Os ages of sulfides (Mo). Errors represent 2σ.

CHAPTER 5

GEOCHEMISTRY OF HYDROTHERMAL FLUIDS

Mineral assemblages, their paragenetic relationships and their spatial distributions, have been used in previous sections to define the three different hydrothermal stages of the Escondida porphyry copper deposit. This chapter investigates the properties of the fluids that transported and deposited the mineral assemblages of each hydrothermal stage and reviews possible effects such properties had on the ability of fluids to transport and deposit metals. The discussion of the ability of the hydrothermal fluids to transport and deposit metals begins with a review of fluid inclusion data, followed by a discussion of sulfur and fluid sources using stable isotope data.

Goal

Fluid Inclusion Study

The goal of this fluid inclusion study is to constrain the trapping pressures, temperatures, and chemistry of the fluids associated with each of the different hydrothermal stages recognized at the Escondida deposit. The data recorded from fluid inclusions include: 1) homogenization temperatures (T_h) either of the vapor phase (Th_V) or of the liquid phase (Th_L), 2) final ice dissolution temperature (Th_{ice}), 3) eutectic temperature (T_e), 4) liquid-to-vapor ratio (L:V), 5) shape and size of fluid inclusions, 6) composition and shape of mineral hosts, and 7) composition and melting temperature of daughter minerals. In addition, the types and likely compositions of solid inclusions present were determined.

Equipment

The microthermometric data were collected using a Fluid Inc.-adapted U.S.G.S. gas-flow fluid inclusion stage (Werre et al., 1979) at the University of Arizona. Calibration of the heating-freezing stage was performed using synthetic fluid inclusions. Accuracy of the equipment is considered to be $\pm 0.2^{\circ}$ C for low temperatures (< 0°C) and $\pm 1^{\circ}$ C for high temperatures (>100°C). Heating and freezing temperatures were recorded with a precision of $\pm 0.2^{\circ}$ C or better and were determined by repeated measurements of fluid inclusions. The exact moment of phase changes in vapor-rich fluid inclusions (see below) was difficult to observe; therefore, poor precision is assigned to these values.

Methods

Fluid inclusion petrography was carried out on 20 samples collected across a vertical interval of 800 m in drill holes and in the walls of the open pit representing all vein-mineral associations found at the Escondida deposit. A total of 480 homogenization and melting temperatures were measured in seven selected sections (Fig. 30). Fluid inclusions occur in hydrothermal quartz, quartz phenocrysts, and sphalerite. The majority of the fluid inclusions measured were hosted by hydrothermal quartz; few were hosted by quartz phenocrysts. The sizes of the fluid inclusions ranged from less than one micron to 60 microns. Most of the heating and freezing work was done on fluid inclusions in the 7-to-20 micron range.

Detailed petrographic and mineragraphic work was conducted on all thin sections to establish mineral paragenesis and the characteristics of the associated fluid inclusions. Necking down of fluid inclusions is not a common feature found in samples from Escondida, but fluid inclusions were rejected where necking down was suspected. All sections were searched were evaluated for CO₂, but it was never detected. Every thin section was searched for primary fluid inclusions photos were taken of all detected primary fluid inclusions; and the thin-section glass was marked for further work. In addition, chips with different types of secondary fluid inclusions were selected for temperature measurements. In this work, primary fluid inclusions are only those inclusions trapped during crystal growth as outlined by Roedder (1984), Bodnar et al. (1985b), and Goldstein and Reynolds (1994) (Fig. 29). All other fluid inclusions are grouped as non-primary fluid inclusions in the graphs (Figs. 31 to 35).

Heating and freezing data were recorded only from fluid inclusion assemblages (FIA's), which represent groups of inclusions of variable sizes and shapes with more than 90 percent of the homogenization temperatures falling within 15°C interval and a consistent vapor-to-liquid ratio (Goldstein and Reynolds, 1994). In this study FIA's are composed of at least three fluid inclusions. The first step was to measure temperatures in all primary fluid inclusions. A total of 124 primary fluid inclusions was measured in 35 FIA's. The second step was to measure non-primary fluid inclusions in all the selected thin section chips. Temperatures of homogenization were always measured before the freezing temperatures, as recommended by Goldstein and Reynolds (1994).

Types of Fluid Inclusions

Fluid inclusions were typed according to the number and relative proportions of phases present at room temperatures (Nash, 1976). Type I, or liquid-rich, fluid inclusions
(Fig. 29h) contain a liquid (L) that occupies ≥ 50 volume percent of the cavity, plus a vapor (V) bubble, and homogenize by filling to the liquid phase.

Type II, or vapor-rich, fluid inclusions (Fig. 29e) are composed of liquid and a vapor bubble, which occupies a larger volume than the liquid. V:L ratios vary from 9:1 to 6:4, and in some cases the inclusions contained anhydrite and probably hematite as solid phases. They homogenize by filling to the vapor phase.

Type III, or hypersaline, fluid inclusions (Fig. 29d) contain liquid, vapor, and one or more daughter minerals (S) such as halite, among others. Type III inclusions homogenize to the liquid phase either by disappearance of the bubble or by disappearance of halite. The classification of daughter minerals is based on their petrographic characteristics, which are explained in detail by Roedder (1992). The shapes of type III fluid inclusions vary from almost perfect negative crystals to rounded and elongated crystals.

Fluid Composition

The composition of the trapped fluid inclusions can be constrained by the eutectic temperature (Te). This is the temperature recorded when the first liquid appears upon heating a completely frozen fluid inclusion. Crawford (1981) and Roedder (1984) presented experimental data reporting eutectic temperatures for the H₂O-NaCl system of - 20.8° and -21.1° C, and for the H₂O-NaCl-KCl system of -22.8° and -22.9° C. The

Fig. 29: Examples of various types of fluid inclusions found in the Escondida porphyry copper deposit. Transmitted light photomicrographs.

- a) Example of primary fluid inclusion assemblages trapped in a growth zone of an anhedral quartz crystal found in a sample of early quartz-orthoclase-biotite vein.
- b) Example of primary fluid inclusion assemblages trapped in growth zones of a subeuhedral quartz crystal from a sample of the white-sericite quartz hydrothermal event. White spots are probably sericite solid inclusions. Opaque solid inclusions (probably sulfides) also are found within the quartz.
- c) Example of fluid inclusion assemblages trapped in growth zones of an euhedral quartz crystal from a sample of the late advanced argillic hydrothermal stage. The fluid inclusions within the growth zone are primary.
- d) Type III or hypersaline fluid inclusion from a primary fluid inclusion assemblage in a sample of early quartz-orthoclase vein. This fluid inclusion contains halite, vapor, liquid, and unknown opaques (probably hematite).
- e) Type II or vapor-rich fluid inclusion.
- f) Coexisting primary type II and III fluid inclusions from an early quartz-orthoclase vein. Homogenization temperatures are approximately 550°C.
- g) Coexisting secondary type I and type II fluid inclusions located in a sample of the chlorite dark-sericite alteration event. Homogenization temperature is 380°C.
- h) Type I or liquid-rich fluid inclusion.
- i) Coexisting primary type I and type II fluid inclusions from a sample of the quartzwhite-sericite alteration event. Homogenization temperature is 310°C. In this photo there are also opaque solid inclusions (probably hematite) and translucent (probably sericite) solid inclusions within the quartz.
- j) Coexisting primary type I and type II fluid inclusions from a sample of the quartz white-sericite alteration event. Homogenization temperature is 310°C.
- k) Part of a planar array of secondary liquid-only fluid inclusions.



Fig. 29

majority of fluid inclusions from Escondida are smaller than 20 microns. This small size makes it difficult to observe the exact first appearance of fluid and record an accurate measurement of the eutectic point.

Eutectic temperatures in type I fluid inclusions from Escondida (n=60), where the first appearance of fluid was clearly observed, vary between -21° and -23°C, suggesting an H₂O-NaCl or H₂O-NaCl-KCl system. The presence of halite and sylvite daughter minerals in type III fluid inclusions supports the NaCl and KCl dominance in the fluids. The presence of anhydrite, chalcopyrite, pyrite, and unknown opaques in the hypersaline fluid inclusions suggest a more complex system at the time of inclusion formation, probably dominated by NaCl and KCl, but with traces of other elements such as Cu, Fe, Ca, and S. Detailed composition of hydrothermal fluids trapped in fluid inclusions of porphyry copper systems has been presented by Ulrich et al. (2001), and Heinrich et al. (1999), suggesting that the fluid composition is more complex than the simple H₂O-NaCl system. This compositional complexity also may affect any estimation of pressures.

Conditions of Pressure and Depth of Trapping

Temperatures of homogenization and salinities of fluid inclusions trapped during boiling can be used to estimate pressure conditions that prevailed at the time when the fluids were trapped (Roedder and Bodnar, 1980). With the exception of the late liquidrich fluid inclusions and probably some of the early hypersaline fluid inclusions (see below), all hydrothermal stages at the Escondida deposit show evidence of boiling (coexisting type II with type I or type III fluid inclusions). Pressure estimates are based on the experimental data of the H₂O-NaCl system presented by different authors including Sourirajan and Kennedy (1962), Urusova (1975), Bodnar et al. (1985), and Bischoff and Rosenbauer (1986).

Eutectic temperatures of fluid composition from Escondida suggest a system dominated by H₂0-NaCl or H₂O-NaCl-KCl. Thus an approximation of the pressure conditions can be based on the experimental data of the H₂O-NaCl system. Although the discussion of pressures will be conducted in the context of the H₂O-NaCl system, it is important to point out possible differences in pressure estimates that would result from more complex systems than that of the H₂O-NaCl-KCl system.

The pressure information in bars is used to estimate a depth range with values varying between a maximum depth under lithostatic conditions (270 bars/km) and a minimum depth under lithostatic conditions (100 bars/km).

Figure 36 presents the basic information necessary to interpret pressure of trapping for fluid inclusions formed during boiling and under non-boiling conditions (Sourirajan and Kennedy, 1962; Bodnar et al., 1985; Bodnar, 1994; Hedenquist et al., 1998). In the following sections of this chapter the components of these figures are explained in detail, and the application of these figures will be illustrated by examples of the different hydrothermal stages of the Escondida deposit.

Distribution of Fluid Inclusions, Temperatures of Homogenization, and Depth of Trapping of the Different Hydrothermal Stages

Fluid inclusions within igneous quartz "eyes".

Description and Temperatures of Homogenization. Spatially coexisting types III and II secondary fluid inclusions occur in quartz phenocrysts. The highest temperatures on hypersaline fluid inclusions were measured on two non-primary fluid inclusion assemblages (n=8) that homogenized to liquid by vapor disappearance and that are hosted by a quartz phenocryst (Figs. 30 and 37). These high-temperature measurements range

from 660° to 680°C with salinities that vary between 50 and 60 equivalent weight percent NaCl (Fig. 30).

Pressure Estimates. Figure 36 presents the basic information necessary to estimate trapping pressure of fluid inclusions during boiling and under non-boiling conditions (Bodnar, 1994; Bodnar et al, 1985). The thick, continuous, convex-upward curve represents P-T conditions where L+V+H coexist; below this line, only V+H coexist. The thin, continuous curves that extend up and to the right from the L+V+H line represent immiscibility curves along which one phase of a specific salinity fluid separates into two phases: one a low-salinity, low-density vapor phase and the other a high-salinity, high-density liquid phase. The numbers on the immiscibility curves of Figure 36 represent salinities of the high-density liquid phase from 30 to 70 weight percent NaCl.

It is possible to illustrate the use of Figure 36 by estimating pressure conditions of trapping of type III fluid inclusions coexisting with type II fluid inclusions found within igneous quartz "eyes" of the Colorado Grande intrusive phase. In this example the intersection of the 680°C vertical line with the immiscibility curve of 60 weight percent NaCl yields approximately 800 bars, allowing the estimation of a maximum depth of trapping of 8,000 m under hydrostatic conditions and a minimum depth of 3,000 m under lithostatic conditions.

Fluid Inclusions Associated with Hydrothermal Stage A.

Description. With the exception of the advancedd argillic veins hosted by rhyolite, all the samples included in this study contain remnants of quartz from the early hydrothermal Stage A. Spatially coexisting types III and II fluid inclusions are common in quartz from hydrothermal Stage A (Fig. 29f) with irregular shapes (veins 1a, 1b, and

1c in Table 2) commonly broken and cemented by minerals of younger hydrothermal stages. These fluid inclusions all contain halite daughter crystals and commonly host other daughter minerals, including sylvite, anhydrite, chalcopyrite, and a bright red mineral (probably hematite).

Halite exhibits a bimodal distribution: in one group of fluid inclusions, halite crystals represent 40 volume percent of the cavity, whereas in other groups of fluid inclusions, halite represents only 15 volume percent or less. Hypersaline fluid inclusions coexist with type II fluid inclusions that contain a bubble, which occupies more than 70 volume percent of the cavities, and small hematite crystals.

Temperatures of Homogenization. Microthermometric data were obtained from 138 primary and non-primary type III fluid inclusions in quartz veins. Of these measured fluid inclusions, 117 homogenized by halite disappearance and 21 by vapor disappearance. Three type III primary fluid inclusion assemblages, which included 13 fluid inclusions, were detected in samples FI1 (Fig. 29a), where the Colorado Grande intrusive phase is cut by quartz veins from hydrothermal Stage A and is weakly overprinted by the quartz-sericitic event. These type III primary fluid inclusions coexist with type II fluid inclusions. The temperatures of homogenization of the type III primary fluid inclusions vary between 500° and 560°C with salinities ranging from 60 to 67 weight percent NaCl equivalent (Fig. 31); they homogenize by vapor disappearance. Temperature measurement of 21 coexisting type II fluid inclusions (n=21) yielded temperatures of homogenization ranging from 320° to 560°C and salinity values from most below 7 weight percent NaCl equivalent (Fig. 30).

The coexistence of types II and III fluid inclusions within hydrothermal Stage A is unambiguous only in the primary FIA's described above. However, within the non-primary fluid inclusion data, most of the vapor-rich fluid inclusions homogenized at temperatures similar to those of the spatially coexisting hypersaline fluid inclusions. The temperatures of spatially coexisting type II and type III fluid inclusions are presented in the histogram of Figure 30, where the bars with light-gray color represent type II fluid inclusions.

Pressure Estimates. Five subgroups of hypersaline fluid inclusions are separated based on the differences between temperatures of halite melting and vapor disappearance (Figs. 37). In Figure 37, the region above the diagonal line represents fluid inclusions that homogenize to liquid by final halite disappearance, while the lower region corresponds to fluid inclusions that homogenize to liquid by final vapor disappearance.

Pressure estimates are straightforward for the hypersaline fluid inclusions that coexist with type III vapor-rich fluid inclusions and homogenized by vapor disappearance after halite dissolution (Fig. 36). These fluid inclusions homogenize by vapor disappearance after halite dissolution at temperatures ranging from 400° to 560°C with salinities between 40 and 52 weight percent NaCl equivalent. These data indicate





Triangles on the top highlight temperature peaks on the histogram and associated hydrothermal event. FIA's = fluid inclusion assemblages; Ser = sericite; Qz = quartz; Chl = chlorite; Bi = biotite; Anhy = anhydrite; Kfds = orthoclase; Cpy = chalcopyrite; Py = pyrite; Mo = molybdenite. In the histogram: no color = type I; light gray color = type II; and dark gray = type III fluid inclusions. The next five figures separate the temperature-salinity data by hydrothermal stage.



Fig. 31: Hypersaline primary fluid inclusions from a quartz-orthoclase vein.

entrapment pressures between 620 and 400 bars, which represent depths between 2,300 and 1,500 m under lithostatic conditions or depths between 6,200 and 4,000 m under hydrostatic conditions (Fig. 36).

Fluid Inclusions Associated with Hydrothermal Stage B.

Description. Quartz from hydrothermal Stage B occurs as subhedral crystals with one or more faces well developed and contains coexisting type I and type II fluid inclusions (Fig. 29b, g, i, and j). Primary fluid inclusions associated with the white-sericite plus pyrite±chalcopyrite±molybdenite hydrothermal event were recorded in samples FI10, FI11, and FI3c (Fig. 29b). Within samples formed during the white-sericite event, the fluid inclusion sizes vary from <5 to 15 microns and have irregular shapes. Liquid-rich fluid inclusions are more abundant than vapor-rich fluid inclusions. Both type I and type II fluid inclusions often contain small hematite crystals, and the vapor bubbles in type I occupy between 40 and 60 volume percent of the cavities.

Non-primary fluid inclusions were found in the quartz formed as part of the chlorite-sericite and the green-sericite events. A group of non-primary type I (n=30) and type II (n=19) fluid inclusions observed in samples F3b, F110, and in F111 may represent fluid inclusions from this early hydrothermal Stage B event (see Table 2). In sample F3b, early K-feldspar-biotite-anhydrite veins are partially altered to chlorite-sericite plus abundant chalcopyrite±pyrite±molybdenite. Samples F10 and F11 are strongly altered to dark sericite. Shapes, sizes, and liquid-to-vapor ratios from the non-primary fluid inclusion assemblages included in this group are similar to those of the primary fluid inclusion assemblages associated with the white-sericite event described above; however, vapor-rich fluid inclusions are more abundant than liquid-rich inclusions (Fig. 29g).

Temperatures of Homogenization. Temperatures of homogenization measured in the primary type I fluid inclusions (n=52) associated with the white-sericite event range from 270° to 380° C. More than 75 percent of the data measured between 290° and 330° C with the mode at 310° C (Fig. 31). Salinity varies between 3 and 19 equivalent weight percent NaCl. More than 70 percent of the data are between 4 and 9 weight percent NaCl, with the mode at 7 weight percent NaCl (Fig. 31). Non-primary fluid inclusions were also measured (n=74), including type I (n=47) and type II (n=27). Their homogenization temperatures and salinities are similar to those obtained for primary fluid inclusions (Fig. 31).

Temperatures of fluid inclusions associated with the chlorite-sericite and the darksericite hydrothermal event were measured in the type I and type II non-primary fluid inclusions of samples F3b, F10, and F11 (n=49). These temperatures range from 340° to 410°C, with more than 75 percent of the data between 360° and 400°C and the mode at 370°C (Fig. 33). Salinity ranges from 5 to 20 equivalent weight percent NaCl with the mode at 8 equivalent weight percent NaCl (Fig. 33).

Pressure Estimates. Temperatures and salinities measurements of fluid inclusions of the white-sericite assemblage indicate a pressure range from 100 to 210 bars, which under hydrostatic conditions would represent depths of trapping between 1,000 and 2,100 m (Fig. 36).



Fig. 32: Temperature-salinity graph of all data from samples of the white-sericite hydrothermal event. The data include measurements of primary and secondary coexisting liquid-rich and vapor-rich fluid inclusions.



Fig. 33: Temperature-salinity graph of coexisting Type I and Type 2 secondary fluid inclusions (Stage B). From samples with strong dark-sericite chlorite alteration.

Temperatures and salinities of non-primary liquid-rich and vapor-rich fluid inclusions, interpreted here as representative of the fluids associated with the chloritesericite and dark-sericite alteration events, indicate trapping pressures that range from 180 to 250 bars (Fig. 36). These pressures would correspond to 1,800 to 2,500 m under hydrostatic conditions, and 700 to 900 m under lithostatic conditions.

Fluid Inclusions Associated with Hydrothermal Stage C.

Description. Hydrothermal quartz from the advancedd argillic Stage C is euhedral (Fig. 29c) and contains coexisting type I and type II fluid inclusions. Primary type I and type II fluid inclusions were recorded in samples F9a and F9b, which are from veins with banded quartz at the vein margins.

Temperatures of Homogenization. Temperatures of homogenization measured in primary type I fluid inclusions (n=40) from sample F9a (Fig. 34) range from 290° to 350°C with a bimodal temperature distribution; one subgroup has temperatures between 330° and 350°C, and a second subgroup has temperatures ranging from 290° and 310°C. The higher temperature subgroup has a salinity range between 4 and 7 equivalent weight percent NaCl. The lower temperatures subgroup has a bimodal salinity distribution with lower values between 4 and 7 equivalent weight percent NaCl and higher salinities between 16 to 20 weight percent NaCl equivalent (Fig. 34).

Pressure Estimates. Most of the data from primary fluid inclusions of the advanced argillic event indicate pressures between 100 and 150 bars, which under hydrostatic conditions represent depths of entrapment from 1,000 to 1,500 m (Fig. 36).

Secondary Late Liquid-rich-only Linear Arrays of Fluid Inclusions.

Description. Liquid-rich fluid inclusions were observed in sphalerite crystals of the advanced argillic assemblage, and secondary planar arrays of liquid-rich-only fluid inclusion assemblages were observed in most of the samples included in this study (Fig. 29k). For the secondary planar arrays, the host fractures crosscut all previous fluid inclusion assemblages. Most of these fluid inclusions are elliptical, and the vapor bubble occupies less than 30 volume percent of the cavities (Fig. 29h).

Temperatures of Homogenization. Homogenization temperatures from late, type I-only fluid inclusions were measured for samples FI3, FI5, FI7, and FI9a (n=29). Temperatures of homogenization measured in these secondary type I fluid inclusions range from 200° to 300° C, with more than 65 percent of the measurements between 220° and 270° C and a mode at 250° C (Fig. 35). Salinity ranges between 0 and 3 equivalent weight percent NaCl, with a mean value of 2.3 equivalent weight percent NaCl (Fig. 35).

Pressure Estimates. For non-boiling conditions like the late, liquid-rich-only fluid inclusions from Escondida with a temperature mode at 250°C, homogenization temperatures represent a minimum temperature of trapping; the real pressure conditions of trapping are somewhere along the 250 isochore (Fig. 36).

<u>Summary</u>

The fluid inclusion data from igneous quartz and a quartz-orthoclase-bearing vein (primary Type II and Type III) indicate pressures of 800 bars, which indicate maximum and minimum depths of 8,000 m (hydrostatic) and 3,000 m (lithostatic). Subsequently,



Fig. 34: Temperature-salinity graph of coexisting Type I and Type II primary fluid inclusions (Stage C).



Fig. 35: Temperature-salinity graph of secondary liquid-rich only fluid

inclusions. These fluid inclusions were trapped very late in the evolution of the the main sulfide event of the hydrothermal system at Escondida. Therefore, they are probably associated with the advanced argillic hydrothermal Stage C.

the magmatic-hydrothermal system developed hydrothermal Stage A under temperatures between 560° and 500°C and pressures of 300 and 600 bars, indicating hydrostatic maximum depths of 3,000 and 6,000 m and lithostatic minimum depths ranging between 1,100 and 2,200 m.

Temperatures decreased from $>500^{\circ}$ to 270° C between hydrothermal stages A and B. Pressure estimates for hydrothermal Stage B vary between 180 and 250 bars, which indicates depths of entrapment between 2,500 and 1,800 m (hydrostatic) and 750 and 1,000 m (lithostatic). The fluids associated with the late, advanced argillic stage have measured temperatures ranging between 270° and 360°C and indicate pressures between 100 and 150 bars, suggesting depths of entrapment of less than 1,500 m (hydrostatic).

Interpretation

The evolution of the boiling fluid associated with hydrothermal Stage A is shown in Figure 38. Magmatic fluid with a salinity of 5 to 10 equivalent weight percent NaCl exsolved at temperatures of about 700°C. When the temperature decreases to 550°C at a pressure of about 600 bars boiling occurred. Boiling results in a hypersaline solution that has a salinity of 40 equivalent weight percent NaCl and a low-density fluid with salinity less than 7 equivalent weight percent NaCl. Lever-rule estimates for the relative proportions of the two immiscibility phases indicate that more than 80 percent of the fluid partitioned into the vapor-dominated fluid. These data are consistent with studies by

Shinohara and Hedenquist, (1997), who indicate that such phase separations result in more than 90 percent of the original fluid going into the vapor phase.



Fig. 36: **P-T diagram of all fluid inclusion data.** Pressure-temperature diagram indicating trapping conditions for fluid inclusions associated with the advanced argillic and the quartz-sericite hydrothermal events. The graph also includes hypersaline fluid inclusions of Stage A that homogenized by final vapor disappearance. See a more detailed explanation of this graph in the text. Basic components of the diagram are after Bodnar (1994) and Bodnar et al. (1985b).



Fig. 37: Thm versus Thv plot. Halite dissolution versus vapor disappearance within hypersaline fluid inclusions that homogenized to liquid. The diagonal line separates Type III fluid inclusions that homogenized to liquid (IIIa and IIIb subgroups) by halite melting and by vapor disappearance (IIIc, IIId, and IIIe subgroups). See text for discussion of trapping conditions of the different subgroups of hypersaline fluid inclusions separated in this graph.



Fig. 38: System H2O-NaCl and boiling curves for fluids of 0.0 and 7 wt. % NaCl equivalent. a. System H2O-NaCl (after Sourirajan and Kennedy, 1962). An exsolved magmatic solution with salinity on the 5-to-10 wt. % NaCl equivalent range and temperature for about 700°C cool down to 550°C where the fluid boiled at about 600 bars (2.5 km under lithostatic pressure). Resulting hypersaline solution had a salinity of 40 wt. % equivalent, and the low-density fluid a salinity lower than 5 wt. % NaCl equivalent, with vapor-rich fluid probably accounting for more than 90 wt. % of the total exsolved solution. **b.** Boiling curves for fluids of 0.0 and 7 wt. % NaCl equivalent (modified after Sourirajan and Kennedy, 1962). At temperatures of 400°C and lower, the condensed low-density phase of Figure 39a may have boiled, forming coexisting undersaturated liquid-rich and vapor-rich fluid inclusions that mark the transition between stage A and B, where Kdfs-Bt-Anhy altered to Chl-Ser.

Heinrich et al. (2002) presented analytical data about coexisting hypersaline and vapor-rich fluid inclusions from five different porphyry systems. Copper values were consistently higher in the vapor-rich phases, which indicate that these low-density liquid phases are potential mineralizers if the solutions do not escape from the system. Low-density fluids will have a tendency to escape from the system, but structural traps or density barriers may contain the fluids within the system.

I interpret that the transtensional structural regime active during the development of the magmatic-hydrothermal system diminished the loss of the low-density fluids produced by boiling during the development of the potassic event. Below 400°C, the condensed low-density phase unmixed, forming the copper bearing quartz-sericitechlorite mineral assemblage (Fig. 38b).

A magmatic fluid for the quartz-sericite alteration does not preclude the possibility that external, non-magmatic fluids were also mixing with the magmatic fluid. This possible mixing of magmatic and non-magmatic fluids will be further considered in the context of stable isotope data.

The early stages in the evolution of the acid-sulfate system were characterized by quartz deposition during the boiling of a hydrothermal fluid at temperatures between 280° and 340° C. The late fluids in the liquid-only fluid inclusions contained in sphalerite and along fractures in quartz are interpreted as non-boiling and are associated with the deposition of late sulfides in the polymetallic veins of the advanced argillic hydrothermal stage at temperatures between 200° and 280° C.

Sources and Evolution of Sulfur and Hydrothermal Fluids

Introduction

The goal of this section is to investigate sources of hydrothermal fluids and sulfur involved in the development of the different stages of the magmatic hydrothermal system using stable isotope data and temperatures from the fluid inclusion section.

To follow the dynamic evolution of the hydrothermal system, activity-activity diagrams were calculated at two different P-T conditions, 550°C at 600 bars and 450°C at 600 bars, for hydrothermal Stage A associated with the biotite-orthoclase-anhydrite-magnetite-bornite-chalcopyrite assemblage. Calculations at 350°C and 200 bars were carried out for the sericite-chlorite-quartz-chalcopyrite-pyrite-molybdenite assemblage of the second hydrothermal stage, and P-T conditions of 250°C at 100 bars were used for the calculations of phase diagrams for the late advanced argillic stage.

Evolution of Sulfide and Sulfate Species

Sulfur-oxygen activity values for hydrothermal Stage A are depicted in Figure 39 at two different sets of P-T conditions that characterized the biotite-orthoclase-anhydrite-magnetite-bornite-chalcopyrite mineral assemblage described above. P-T conditions follow from the analysis of fluid inclusions. At 550°C and 600 bars (Fig. 39a) chalcopyrite-magnetite-bornite are stable within the stability field of anhydrite at log aO₂ between -19 and -17.8 and log aS₂ ranging from -4.2 to -3.0 (calculated at $mK^+ = 0.1$ and 0.01). At 450°C (Fig. 39b) the same mineral assemblage is stable between -21.7 and $-22.9 \log aO_2$ and -6.2 to $-4.7 \log aS_2$ (calculated at $mK^+ = 0.1$ and 0.01).

Estimated sulfur-oxygen activity and pH values of the second hydrothermal stage

Fig. 39: Log aO₂-log aS₂ and log aO₂-pH diagrams calculated at four different P-T conditions: **39a**. 550°C at 600 bars and **39b**. 450°C at 600 bars showing the characteristic mineral associations of hydrothermal Stage A that include bt-kfds-anhy-mt-bn-cpy. All diagrams for this early hydrothermal stage were calculated with total sulfur of 0.01 molal and 0.1 K⁺ molal. **39c** and **39d**, calculated at 350°C at 200 bars, are characteristic of hydrothermal Stage B that includes ser-chl-cpy-py-mo. The two diagrams of the quartz-sericite stage were calculated with total sulfur of 0.01 molal. Heavy continuous lines separate stability fields of pyrite (py), pyrrhotite (po), magnetite (mt), and hematite (hm) while the thick long-dashed lines represent the transition between sulfur species. Thin long-dashed lines were calculated at constant sulfur content. The thin short-dashed lines represent constant pH and mineral buffers sensitive to pH. Thin continuous lines mark the orthoclase-muscovite, anhydrite-wollastonite, and bn+py-cp transitions. See Appendix E for mineral abbreviations. Equilibrium constants from SUPCRT92 (Johnson et al.,1992),Barton and Skinner (1978), Brimhall (1980); and Jannas (1995).







Fig. 40: Activity-activity (a) and activity-pH (b) diagrams calculated at 250° C at 100 bars representing P-T conditions and hydrothermal mineral associations characteristic of the late advanced argillic hydrothermal Stage. Calculated with total sulfur of 0.01 molal and 0.1 K⁺ molal. The gray areas named IIIa to IIIe represent the different mineral associations observed in veins of this hydrothermal stage. Heavy continuous lines separate stability fields of pyrite (Py), pyrrhotite (Po), magnetite (Mt), and hematite (Hm), while the thick long-dashed lines represent the boundaries of the fields of sulfur species. Thin long-dashed lines were calculated at constant sulfur content of 0.01 and 0.1 molal. The thin short-dashed lines represent constant pH and mineral buffers sensitive to pH. Thin continuous lines mark the orthoclase-muscovite, anhydrite-wollastonite, and bornite+pyrite-chalcopyrite transitions. See Appendix F for mineral abbreviations and Appendix E for mineral reactions and equilibrium constants. Equilibrium constants were calculated with the SUPCRT92 program (Johnson et al., 1992) and data from Barton and Skinner (1979), Brimhall (1980), and Jannas (1995).

are shown in figures 39c and 39d. At 350°C, 200 bars, and $m\Sigma$ S ranging from 0.1 to 0.01 (Montoya and Hemley, 1975), the sericite-quartz-chalcopyrite-pyrite mineral association is stable at oxygen fugacities between -25.2 and -26.2 and log aS₂ in the -5.2 to -3.9 range (Fig. 39c). This mineral association is stable at a pH lower than the orthoclase-muscovite (5.6) buffer, and since sulfate minerals are not observed with this mineral association, the pH is higher than the alunite-sericite stability line (3.9) (Fig. 39d).

Sulfur-oxygen activities and pH values of the latest hydrothermal stage are presented in Figure 40. Sulfide and silicate mineral parageneses of veins of hydrothermal Stage C starts with precipitation quartz-pyrite-enargite (C-a) and continues with the deposition of bornite-chalcopyrite-pyrite (C-b), which is followed by the precipitation of sphalerite-pyrite (C-c) and by the later deposition of chalcocite-covellite (C-d). All of these sulfides were deposited under conditions where sericite and pyrophyllite were stable, while alunite was absent. The last mineral association in veins of the advanced argillic event contains pyrite±galena and alunite (C-e). At a total sulfur content ($m\Sigma S$) of 0.01 and assuming K⁺ constant, this mineral paragenesis indicates aO₂ values ranging from -35.7 to -32.8 (Fig. 40). The pyrophyllite-sericite and the alunite-sericite mineral buffers constrain the pH close to 3.5 (Fig. 40b).

Sulfur Isotope Data

The δ^{34} S values of chalcopyrite from hydrothermal Stage A range from -3.2 to -2 per mil, whereas two values measured on anhydrite are +19.6 and +19.9 per mil (Table 6, Figs. 41 and 42). A fractionation factor between anhydrite and chalcopyrite ($\Delta_{anhy-cp}$) of 21 to 23 represents a temperature of approximately 400° C ± 25, which coincides with the

Esc7 ahny-cpy A 16.9 -2.9 384 ± 25 400	
Esc7 ahny-cpy A 16.9 -2.9 384 ± 25 400)
Esc8 ahny-cpy A 16.6 -2.0 406 ± 25 420	
Esc9 bt-kfds-qz A -2.3	
Esc10 bt-kfds-qz A -3.2	
Esc14 Green ser B(a) -0.8	
Esc15 Green ser B(a) -0.6 360	-380
Esc16 Green ser B(a) -1.1	
Esc17 chl-ser B(a) -0.7	
Esc18 White ser B(b) -0.5	
Esc19 White ser B(b) -0.4	
Esc20 White ser B(b) 0.7 -0.5 339 ± 70 340)
Esc21 White ser B(b) 0.2	
Esc22 py-en C(a) -0.2	
Esc23 py-en C(a) -0.1	
Esc24 py-sf C(c) -1.3 -2.5 229 ± 90 250)
Esc25 py-ga-alu C(d) 15.0 -0.1 2.7	
Esc27 py-alu C(d) -2.0 0.2	
Esc28 py-ga-alu C(d) 7.7 -3.1 >1000 ± 25	
Esc29 py-alu C(d) 0.3	

 Table 6.
 Sulfur isotope data.

Temp. F.I are the measured temperatures of fluid inclusions. Isotopic temp. represents the calculated temperatures from mineral pairs. For mineral abbreviations see Appendix E.

temperature indicated by fluid inclusions in the same sample containing the association anhydrite-chalcopyrite (Table 6). This agreement of temperature values indicates that Sisotopic equilibrium was reached during the development of the early hydrothermal stage. The δ^{34} S values of chalcopyrite from hydrothermal Stage B range from –1.1 to –0.6 per mil within the dark-sericite veins and between –0.5 to 0.7 per mil within the white-sericite veins (Table 6, Fig. 41).

The δ^{34} S values of early pyrite from hydrothermal Stage C lie close to -0.2, while in the sphalerite-pyrite mineral association, δ^{34} S values are -1.3 (pyrite) and -2.5 (sphalerite) per mil. Within the alunite-bearing veins, the values δ^{34} S of pyrite range from -3.1 to +0.2 per mil. The only measured value from galena is +2.7 per mil.

The δ^{34} S values of alunite range widely: three specimens yielded -2, +7 and +15 per mil. Only the alunite samples close to +15 per mil present textural characteristics interpreted to be clearly of hypogene origin. These characteristics include pinkish color and replacement textures after the feldspar minerals along vein wall. The other two alunite samples with δ^{34} S values of +7 and -2 are white and fine-grained alunite contained within the sulfide veins. They could have either a hypogene or a supergene origin. Fractionation factors among alunite and sulfides yielded temperatures higher than 1,000°C, which indicates that isotopic equilibrium was not reached in the temperature ranges considered.

The calculated isotopic temperature for the pyrite-sphalerite mineral pair is 229° C \pm 90, very close to the measured temperature of liquid-rich-only fluid inclusions (250°C),



Fig. 41: Histogram of δ^{34} S (‰) values of sulfides from the different hydrothermal stages of the Escondida deposit. For mineral abbreviations see Appendix E.



<u>Fig 42</u>: Histogram of δ^{34} S (‰) values of sulfates from the different hydrothermal stages of the Escondida deposit. For mineral abbreviations see Appendix E.

suggesting that sulfur species equilibrium was reached among sulfides during the deposition of pyrite and sphalerite.

Oxygen-Hydrogen Isotope Data

The calculated oxygen and hydrogen isotopic composition of the fluid that was in equilibrium with silicate mineral assemblages of hydrothermal Stage A is typical of magmatic values (Fig. 43). The composition of water that was in equilibrium with igneous quartz and biotite ranges from -32 to -52 per mil δD (avg. -45 %; n = 6), and the $\delta^{18}O$ value averages 6.3 per mil (Fig. 43).

The composition of water was calculated at 700°C based on the highest temperature measured in igneous quartz. The composition of water that was in equilibrium with hydrothermal biotites (pervasive and vein controlled) calculated at 550° C ranges between -32 and -52 per mil δ D (avg. -45 %; n = 6). Their δ^{18} O value averages 6.3 per mil (Fig. 42), which is probably lower than its original value, owing to weak chloritization. The δ^{18} O value of igneous quartz from igneous rocks and quartz from veins associated with the high-temperature hydrothermal Stage A is in agreement with the δ^{18} O value of biotites.

Sericite samples collected from samples of dark and white sericite have compositions that result in calculated water numbers close to the values of the hydrothermal biotites when 350° C is used in the calculation, and slightly outside the field of magmatic waters when 280° C is used in the calculation (Fig. 43). These values are in agreement with the δ^{18} O values of quartz from samples of sericite-bearing veins (Fig.43).

			Measured		Calculated		
Sample no.	Event	Mineral	δ ¹⁸ O ‰	δD‰	δ ¹⁸ O‰	δD‰	Temp.
Esc1	lgnQz	Quartz	7.93		7.238766		700
Esc2	lgnQz	Quartz	8.92		8.228766		700
Esc4	lgnQz	Quartz	8.56		7.868766		700
Esc5	lgnQz	Quartz	8.27		7.578766		700
Esc6	lgnQz	Quartz	8.66		7.968766		700
Esc22	AdvArg	Quartz	9.11		3.932201		280
Esc11	Wser	Quartz	9.28		4.102201		300
Esc12	Chl-Ser	Quartz	9.17		5.243633		380
Esc8	Kfd-Bt-Ahy	Quartz	8.97		7.224268		550
Esc13	a2Qz	Quartz	9.12		7.374268		550
Esc14	Gser	Sericite	6	-88.5	4.155053	-63.5	380
Esc15	Gser	Sericite	7.795	-87.4	5.950053	-62.4	380
Esc16	Gser	Sericite	6.635	-79.6	4.790053	-63.1	380
Esc17	Gser	Sericite	6.56	-85	4.715053	-60	380
Esc18	Wser	Sericite	7.63	-83	4.59345	-58	300
Esc19	Wser	Sericite	8.39	-99.4	4.870716	-74.4	300
Esc20	Wser	Sericite	7.56	-80	4.040716	-55	300
Esc7	Biotite	Biotite	2.78	-94.2	5.289445	-59.9529	550
Esc8	Biotite	Biotite	2.82	-91.3	5.329445	-57.0529	550
Esc9	Biotite	Biotite	3.43	-85.6	6.005154	-51.3529	550
Esc1	IgnBiotite	Biotite	3.91	-100.9	6.587493	-66.6529	700
Esc2	IgnBiotite	Biotite	3.89	-94.3	6.6	-60.0529	700
Esc5	IgnBiotite	Biotite	3.76	-81.9	6.51	-47.6529	700
Esc22	Kaolinite	Kaolinite	16.59	-89.9	8.949662	-75.006	280
Esc23	Kaolinite	Kaolinite	12.29	-93.7	8.512352	-78.806	280
Esc24	Illite	Illite	13.49	-81.9	8.512352	-55	300
Esc25	Illite	Illite	13.15	-81	8.172352	-56.9	300

Table 7: **Oxygen and hydrogen data.** Measured δ^{18} O and δ D data of igneous and hydrothermal minerals and calculated δ^{18} O and δ D of coexisting water.

Gser = dark sericite; Wser = white sericite; ign = igneous; Qz = quartz; Temp. = temperature.



Fig. 43: δD (%) versus $\delta^{18}O$ (%) diagram for the calculated isotopic composition of H₂O in equilibrium with the alteration minerals over the range of temperatures measured in fluid inclusions. Also given are the oxygen isotope compositions of H₂O in equilibrium with igneous and hydrothermal quartz. Meteoric and primary magmatic water values from Taylor (1979).

Samples of illite, kaolinte, and quartz from veins of the late advanced argillic hydrothermal Stage C were handpicked and analyzed for oxygen and hydrogen. The results are presented in Table 7 and Figure 42. Samples of illite came from veins found on the east wall of the Escondida open pit at the 2,800 bench (Dec. 1996), and the samples of kaolinite were collected from a drill hole in the bottom of the pit at a depth of 800 m below the pre-mining surface.

Oxygen and hydrogen isotope values of the fluids associated with this acid-sulfate event were calculated at 250°C. The quartz sample of the advanced argillic event has a lighter δ^{18} O value than those of illite and kaolinite, which implies that water in equilibrium with these clay minerals was magmatic. However, if quartz, kaolinite, and illite formed at the same temperature, the quartz is the more likely to preserve the original δ^{18} O signature. Illite and kalolinite fill cavities within the quartz-sulfide veins and may have formed very late in the evolution of the advanced argillic event or could be related to the supergene event. Therefore, their closure temperature could be lower than the minimum temperature measured in quartz from the advanced argillic assemblage (200°C). If calculations are made using 150° and 50°C for illite and 100° and 50°C for kaolinite (Fig.42), the δ D and δ^{18} O values move toward the meteoric water line. The calculated δ D and δ^{18} O numbers are close to -65 per mil δ D and -9 δ^{18} O, which are very close to the calculated values of meteoric water associated with the hydrothermal system of the 41 Ma El Salvador porphyry copper deposit (Watanabe and Hedenquist, 2002).

Discussion and Interpretation of Hydrothermal Evolution

 δ^{18} O and δ D isotope results indicate the dominant influence of magmatic water during the evolution of hydrothermal stage A. The transition from the orthoclase-biotiteanhydrite-bearing assemblages of Stage A to the quartz-dark-sericite-chlorite assemblage of hydrothermal Stage B occurred close to 400°C. With temperatures falling from 380° to 280°C, the calculated δ^{18} O and δ D values of fluids in equilibrium with the dark-sericite and the white-sericite still are close to those of magmatic water but show some shift toward the meteoric water.

Sulfur isotope data also support a magmatic source for sulfur associated with hydrothermal stages A and B. The δ^{34} S values from hydrothermal Stage A vary between -3.2 and -2 per mil in chalcopyrite and are close to +19.5 per mil in anhydrite (Table 6). The general temperature correspondence between fluid inclusion measurements and sulfur isotope estimations suggests that isotopic equilibrium was reached during the development of the early hydrothermal stage. δ^{34} S from sulfides of Stage A are the lowest values measured in this study and may interpreted as follows:

With falling temperatures, the SO_2 partitioned to H_2S and H_2SO_4 on a 1-to-3 ratio indicated by the following reaction (Ohmoto and Rye, 1979):

$$4SO_2 + 4H_2O = H_2S + 3H_2SO_4$$

The excess of H_2S may have resulted in precipitation of sulfides, while H_2SO_4 promoted the deposition of anhydrite that tends to deplete the solution in $\delta^{34}S$ (Jensen, 1959). This process would be effective only if precipitation removes more sulfate than sulfide. Otherwise the effect would be the opposite, decreasing reduced:oxidized ratio as temperatures fall. The δ^{34} S values of chalcopyrite and pyrite from hydrothermal Stage B range from -1.1 to -0.6 per mil within the dark-sericite event and between -0.5 to 0.7 per mil within the white-sericite veins.

The observed paragenesis in veins of the advanced argillic event suggests continued oxidation of the system at a pH close to 2.6 or 3.5. The δ^{18} O and δ D data from quartz, illite, and kaolinte suggest the mixing of a magmatic source with a meteoric water source.

The δ^{34} S from the early pyrite-enargite (C-a) and sphalerite-pyrite (C-c) mineral associations without alunite present values close to zero within a narrow range from –2.5 to –0.1, respectively. On the other hand, the δ^{34} S from sulfides associated with the alunite-bearing mineral association (C-d) are more variable than the early sulfide phases. The δ^{34} S values from sulfides of the alunite-bearing veins range from –3.1 in pyrite to +2.7 in galena.

The advanced argillic mineral association postdates the early potassic and the quartz-sericite hydrothermal stages and the emplacement of rhyolite intrusions, which also postdate the two early hydrothermal stages. The crosscutting relationships among different intrusive rocks and veins in association with sulfur isotopic data is used to consider the evolution of these late acid-sulfate mineral assemblages and their sources of heat, fluid, and sulfur.

Advanced argillic systems have been interpreted to form by a magmatic vapor that condensed by mixing with meteoric water at shallow levels or by the circulation of heated, acid meteoric waters (White, 1991). At Escondida the circulation of heated, acid meteoric waters may have been favored by the intrusions of rhyolitic magmas or late barren rhyo-dacitic dikes. Both intrusive events postdate the development of potassic and quartz-sericite events and potentially may have heated surface water that leached metals from earlier mineralization. If the sulfur contained in the fluid responsible for the acid-sulfate event came from the leaching of previous sulfides, the δ^{34} S could not be higher than the source. As noted in Figure 41, the δ^{34} S values of hydrothermal Stage B are higher than those of hydrothermal Stage A, and therefore it seems unlikely that sulfides from Stage B were formed by the leaching of earlier sulfides. The broad distribution of δ^{34} S from sulfides of the advanced argillic event suggests that part of the sulfides associated with this late mineralizing stage may have formed from the leaching of sulfides from the two earlier mineralizing events. This conclusion is supported by the light δ^{34} S value of the hypogene alunite (15 per mil) that may have been inherited from the leaching of early anhydrite. Some δ^{34} S values from sulfides of the advanced argillic event are higher that those of the two early mineralizing events, suggesting an external introduction of sulfur with values close to zero, which may be related to a SO₂ magmatic plume that was absorbed by heated surface meteoric water to form the advanced argillic hydrothermal stage.

CHAPTER 6

GEOCHEMISTRY OF IGNEOUS ROCKS

Trace-and major-element geochemistry of igneous rocks from the Escondida district have been presented by Marinovic et al. (1992) and by Richards et al. (2000). This study adds Sm-Nd and Rb-Sr data and trace-and major-element analysis from the Paleozoic rhyolitic basement and the Paleocene andesite to the regional database. It also includes trace-and major-element analysis, in addition to Sm-Nd, Rb-Sr and oxygen isotope data of the different intrusive rocks present in the Escondida and the Escondida Norte deposits. Re-Os isotopic data of magnetite from the intrusive rocks of the Escondida deposit are also discussed in this chapter.

Sample Selection, Preparation and Analysis

The location and analytical results of samples published by Richards et al. (2001) and the samples analyzed in this dissertation are presented in Table 8. The geochemical database of the Escondida region presented by Richards et al. (2001) contains a large number of samples from the Paleozoic basement and Late Eocene-Oligocene diorite from the district. The samples analyzed in this study are mainly from the Escondida (six samples) and the Escondida Norte (two samples) deposits. In addition, one Tertiary andesite sample and one Paleozoic rhyolite sample were analyzed.

The 10 samples of this study were selected from the least-altered rocks from outcrops, open pit walls, and drill core. All 10 samples were prepared for analysis in the Department of Geosciences of the University of Arizona. These samples were sawed to remove any macroscopic evidence of alteration; later they were crushed and powdered. Quartz "eye" and biotite igneous crystals from the different igneous rocks were hand picked, and igneous and hydrothermal magnetite samples were isolated by magnetic separation.

The whole-rock, trace-and major-element analyses were run in the laboratories of XRAL in Toronto, Canada. Oxygen isotope analyses of igneous quartz and biotite crystals were carried out at the Southern Methodist University in Dallas, Texas. The Re-Os analyses of magnetite samples were performed by Ryan Mathur in the laboratory of Dr. J. Ruiz at the University of Arizona. The Sm-Nd and Rb-Sr analyses were carried out by Clark Isachsen in the laboratory of Dr. J. Patchett, also at the University of Arizona.

The samples of the Colorado Grande and the Escondida intrusive phases (D71 = Esc1 and RD1246=Esc2) of the Escondida stock and samples from the Cerro-Sureste rhyolite (Rhy2=Esc5) present loss of ignition numbers (LOI) close to 1.0 percent (Table 8). Weak chloritization of biotites was observed with the microprobe. The sample of the granodiorite dike or phase 3 of the Escondida stock (GdD=Esc3) is altered to quartz-sericite with loss of ignition of 4.25 percent. The samples of the rhyolitic dome (Rhy1=Esc4) and the late barren rhyodacitic dike (LD=Esc6) are moderately silicified and argillized with loss of ignition numbers of 3.2 and 5.35, respectively. The Tertiary andesite (And=Esc30), correlated with the Paleocene Augusta Victoria Formation, shows weak propylitic alteration with LOI=2.65 percent, whereas the Paleozoic rhyolite (PzRhy=Esc00) is relatively fresh, with LOI=1.9 percent (Table 8).
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Sample	ESCN1 ¹	ESCN21		Esc10 ¹	Esc1 ¹	Esc2 ¹	Esc3'	Esc4 ¹	Esc5 ¹	Esc6 ¹	SGAnd3	IM40	IM43	IM58	IM85	IM86	ZAL2	ZAL3	IM72	IM88	IM89	IM95	IM96
Rock Type	Tgn.	Tgn.	And	Pzrhy	Tgn.	Tgn.	Tgn.	Trhy	Trhy	Trhy-dac	Tand	Pzrhy	Pzand	Pzand	Pzrhy	Pzrhy	Pzrhy	Pzrhy	Tkand	Tkand	Tkrhy	Tkrhy	Tkand
SiO2	65.6	65.4	62.2	69.8	68.5	69.7	71.1	77.2	69.8	71.4	54.2	70.9	61.8	60.7	63.6	64.4	78.6	74.4	53.1	54.6	73	74.2	52.8
TiO2	0.591	0.498	0.587	0.418	0.39	0.302	0.304	0.332	0.277	0.326	0.92	0.48	0.64	0.83	0.69	0.67	0.18	0.59	0.69	0.99	0.15	0.15	0.97
AI2O3	18.9	16.5	16.7	14.3	16.3	16.3	16.3	14	16.7	17.7	17	14.2	15.8	22.6	16.1	15.6	11.3	14.6	17.8	16.8	13.6	13.7	17.6
Fe2O3	3.09	4.84	5.03	2.78	2.27	2.09	3.22	1.08	1.95	1.26	4.98	3.53	5.83	8.11	5.66	5.33	1.42	1.72	7.99	7.56	1.01	0.93	8.1
MnO	0.01	0.02	0.06	0.06	0.02	0.03	-0.01	-0.01	0.05	-0.01	2.5	0.07	0.1	0.03	0.1	0.1	0.02	0.02	0.16	0.14	0.03	0.06	0.15
MgO	0.45	1.52	3.16	0.8	1.03	0.78	0.3	0.26	0.63	0.36	0.19	0.63	2.88	0.64	2.41	2.27	0.2	0.34	6.1	5.97	0.49	0.42	6.34
CaO	0.61	2.62	4.03	1.74	2.56	2.96	0.07	0.1	0.68	0.06	4.78	1.2	4.1	0.97	4.25	3.66	0.06	0.07	7.55	5.97	1.13	2.23	6.86
Na2O	4.17	4.91	3.77	4.34	5.17	4.89	0.53	0.21	4.29	0.91	7.27	3.38	2.87	1.11	3.18	3.55	1.39	1.91	2.75	3.51	1.37	1.47	2.88
K2O	2.33	2	1.65	3.49	2.47	2.42	3.66	3.28	3.19	2.57	3.73	4.19	3.36	2.83	2.53	2.63	2.82	2.09	0.83	1.07	3.06	2.41	0.66
P2O5	0.17	0.11	0.21	0.09	0.15	0.12	0.11	0.13	0.11	0.08	3.01	0.11	0.13	0.12	0.17	0.16	0.03	0.06	0.12	0.26	0.03	0.04	0.31
LOI	3.75	0.8	2.65	1.9	0.8	0.6	4.25	3.2	1.45	5.35	1.3	1.02	1.86	1.43	1.38	1.4	2.38	3.75	2.33	2.34	2.62	3.72	2.62
La	18	23.6	31.1	37.5	22.7	39.2	21.7	26.6	15.9	18.8	13	34.9	20.8	28.7	21.7	22.4	25.6	32.7	8.72	14.8	6.04	7.08	16.3
Ce	33.2	44.4	62.7	77	46.1	72.6	35.5	45.7	28.7	32	27	70.9	43.4	49	4.82	46	53	66.6	18.8	31.6	14.4	15.8	36.1
Nd	12.7	18	28	35	19	29.7	11.6	16.2	13.8	12.5	16	30	18.3	23.8	20.5	21.2	20.1	28.3	9.97	16.3	5.6	6.64	18.3
Sm	2.5	3.1	5.5	6.9	3.9	4	1.3	1.9	2.4	2.3	3.8	6.22	3.84	5.7	4.33	4.37	3.88	5.57	2.56	3.7	1.89	2.03	4.09
Eu	0.76	0.9	1.25	1.35	0.96	1	0.47	0.69	0.77	0.63	0.9	1.48	0.85	1.54	1.01	1.02	0.54	1.35	0.82	1.09	0.13	0.17	1.19
Gd	2.9	2.4	4.6	6.9	2.7	2.7	1	1.3	2	1.7	4	5.5	3.47	5.22	4.03	3.96	3.43	4.66	2.55	3.51	2.16	2.11	3.82
Dy	2.1	1.8	4	6.1	1.4	1.6	0.2	0.6	1	0.9	4.4	5.19	3.57	3.85	3.76	3.75	3.59	4.63	2.54	3.5	3.37	3.01	3.6
Er	1.3	1	1.9	3.8	0.7	0.9	0.3	0.3	0.5	0.8	2.71	3.13	2.13	2.06	2.28	2.28	2.43	2.74	1.52	1.99	2.16	1.92	2.02
Yb	1.2	1	2.1	3.7	0.7	0.9	0.3	0.3	0.5	0.7	2.3	3.26	2.25	2.2	2.13	2.22	2.79	2.89	1.55	1.87	2.25	1.96	1.83
Y	11	10	19	37	7	8	1	3	5	4		29.7	21.2	19.8	22.3	22.5	22.5	26.7	15.5	19.2	21.6	19.2	19.7
Ho	0.37	0.35	0.68	4.38	0.28	0.33	0.05	0.11	0.18	0.22	0.8	1.1	0.75	0.77	0.8	0.78	0.79	0.98	0.55	0.71	0.74	0.66	0.73
Lu	0.2	0.15	0.33	0.61	0.1	0.15	0.05	0.05	0.08	0.14	0.34	0.47	0.31	0.32	0.35	0.36	0.42	0.44	0.21	0.28	0.33	0.28	0.27
Pr	3.5	5.2	7.5	9.5	5.3	8.2	3.6	4.7	3.7	3.6		8.08	4.88	6.09	5.25	5.35	5.67	7.38	2.37	3.9	1.63	1.96	4.39
Tb	0.4	0.3	0.7	1.2	0.3	0.3	0.1	0.2	0.2	0.2		0.81	0.58	0.68	0.6	0.58	0.55	0.72	0.4	0.54	0.49	0.45	0.58
Th	6	7.5	8.5	14.9	4.7	6.9	6.2	6.4	3.7	4		11.8	14.1	19	5.59	6.4	11	9.77	2.37	1.62	9.8	8.43	1.91
U	6.2	1.7	1.9	3.2	1.1	1.3	1.1	1.3	1.1	0.8		2.99	3.81	2.33	1.61	1.66	1.86	2.01	0.68	0.45	4.93	3.7	0.49
Eu/Eu	0.86	1.01	0.76	0.60	0.90	0.93	1.26	1.34	1.07	0.97	0.71	0.77	0.71	0.86	0.74	0.75	0.45	0.81	0.98	0.93	0.2	0.25	0.92
La/Yb	10.76	16.93	10. <u>6</u> 0	7.27	<u>23.2</u> 6	31.2 <u>4</u>	51.8 <u>8</u>	63.60	22.81	19.26	4.05	7.68	6.64	9.36	7.29	7.22	6.59	8.12	4.04	5.69	1.93	2.59	6.39

 Table 8. Major-and trace-element data from igneous rocks from the Escondida region. The 10 samples with superscript (1) are from this work (in bold), SGAnd is from Williams (1992), and all other samples are from Richards et al (2001).

Table 8. Continued.

IM98	Sample	IM122	IM156	IM158	1M159	1M128	1M8	IM10	IM61	IM62	IM68	IM69	IM70	IM79	IM81	IM90	IM110	IM116	IM14
Tkrhy	Rock Type	Tkrhyolite	Gabbro	Gabbro	Gabbro	Tand	Diorite	Anddike	Diorite	Dacite	Diorite	Dacite	Diorite						
74.3	SiO2	73.42	44.76	45.63	45.28	54.46	58.25	59.69	54.62	59.12	58.77	56.64	59.23	62.82	55.15	63.12	57.89	65.19	59.87
0.09	TiO2	0.08	1.13	1.74	1.87	0.82	0.74	0.77	0.96	0.76	0.91	0.95	0.7	0.59	0.91	0.6	0.76	0.56	0.88
12.7	AI2O3	12.26	18.9	17.55	19.85	17.69	16.95	17.27	18.01	17.98	18.01	17.87	17.49	16.39	18.45	17.4	16.85	16.21	18.47
0.51	Fe2O3	0.52	6.95	11.32	11.56	7.34	5.41	5.44	6.83	6	6.11	6.73	5.68	3.78	6.1	3.67	5.84	4.03	6.35
0.06	MnO	0.07	0.11	0.08	0.13	0.11	0.1	0.09	0.12	0.12	0.1	0.12	0.11	0.1	0.12	0.07	0.1	0.1	0.12
0.21	MgO	0.14	7.44	6.18	5.35	3.49	2.58	2.95	4.57	2.94	3.46	4.11	2.75	1.56	3.42	1.76	3.37	1.98	2.88
0.65	CaO	0.45	13.13	8.18	10.71	7.91	5.97	5.77	6.76	6.42	6.72	7.45	5.72	4.14	7.76	4.18	5.86	3.61	6.49
4.6	Na2O	4.77	1.5	3.38	2.82	2.88	3.64	3.37	3.46	3.77	3.51	3.17	3.5	3.95	3.33	4.58	3.17	3.75	3.65
3.02	K2O	3.02	1.79	1.62	0.96	1.54	1.93	2.03	1.21	1.56	1.49	1.53	1.84	2.63	1.11	2.25	2.59	3.34	1.3
0.02	P2O5	0.02	0.15	0.6	0.23	0.27	0.28	0.27	0.3	0.29	0.3	0.27	0.27	0.24	0.31	0.24	0.24	0.19	0.3
3.7	LOI	3.75	3.5	2.84	0.77	2.36	0.29	1.49	2.65	0.13	1.11	0.31	1.72	1.21	2.22	1.27	1.51	1.42	0.2
6.84	La	6.63	7.97	19.23	10.13	19.65	23.28	22.33	16.85	20.01	20.15	20.51	22.32	23.88	19.41	22.26	24.05	25.88	19.8
15.6	Ce	15.48	17.66	43.45	20.4	40.05	47.13	45.5	36.1	41.14	41.04	42.27	44.78	46.68	40.95	44.83	48.77	51.14	41.46
5.87	Nd	5.53	10.19	23.68	11.02	19.44	21.85	20.82	19	18.77	19.24	20.6	20.45	19.8	20.96	18.82	21.65	20.93	20.12
1.61	Sm	1.66	2.6	5.34	2.55	4.13	4.08	3.95	3.85	3.67	3.84	4.26	3.89	3.54	4.08	3.47	4.41	3.76	4.14
0.13	Eu	0.12	0.96	1.53	1.26	1.22	1.17	1.1	1.22	1.07	1.16	1.24	1.11	0.98	1.16	0.97	1.1	0.97	1.26
1.79	Gd	1.75	2.63	5.28	2.52	3.48	3.48	3.18	3.36	3.17	3	3.72	3.17	2.4	3.2	2.49	3.66	3.07	3.54
2.48	Dy	2.41	2.27	4.45	2.12	3.07	2.56	2.4	2.55	2.46	2.33	2.93	2.54	1.73	2.2	1.45	2.95	2.35	2.9
1.68	Er	1.55	1.15	2.32	1.11	1.57	1.37	1.33	1.28	1.29	1.22	1.54	1.34	0.86	1.08	0.73	1.6	1.28	1.51
1.79	Yb	1.66	0.96	2.18	0.92	1.55	1.28	1.23	1.12	1.15	1.05	1.37	1.39	0.78	0.97	0.6	1.52	1.3	1.48
17.1	Y	15.95	12.11	24.04	12.38	17.1	12.28	14.27	14.25	14.98	12.85	16.81	14.77	11.16	13.38	9.53	17.72	14.56	16.77
0.55	Ho	0.53	0.45	0.85	0.41	0.59	0.5	0.46	0.5	0.48	0.44	0.56	0.51	0.34	0.42	0.27	0.58	0.46	0.58
0.25	Lu	0.25	0.15	0.34	0.13	0.23	0.2	0.19	0.17	0.18	0.15	0.22	0.24	0.12	0.14	0.1	0.24	0.2	0.22
1.73	Pr	1.75	2.29	5.58	2.53	4.82	5.45	5.32	4.58	4.79	4.91	5.04	5.28	5.34	5.08	5.17	5.58	5.65	4.99
0.37	Tb	0.34	0.39	0.72	0.35	0.52	0.41	0.4	0.43	0.4	0.42	0.49	0.42	0.33	0.39	0.26	0.49	0.38	0.49
8.99	Th	8.95	1.28	2.78	0.97	4.03	4.62	5.11	1.87	3.39	3.61	3.94	4.13	5.83	1.96	3.48	12.17	13.11	3.79
4.25	U	4.13	0.27	0.5	0.28	1	0.87	1.31	0.45	0.78	0.91	0.87	0.84	1.39	0.46	1.04	3.4	2.79	0.63
0.23	Eu/Eu	0.215	1.122	0.881	1.52	0.984	0.949	0.949	1.037	0.959	1.045	0.952	0.966	1.028	0.981	1.009	0.837	0.873	1.006
2.74	La/Yb	2.865	5.955	6.327	7.898	9.094	13.046	13.022	10.792	12.481	13.765	10.739	11.518	21.96	14.353	26.612	11.349	14.28	9.596

Table 8. Continued.

IM45	IM46	Sample	IM47	IM50	IM52	IM53	IM55	IM59	IM60	IM119	IM143	IM149	IM150	IM151	IM154	ESC1	ESC3	ZAL1
Diorite	Diorite	Rock Type	Diorite	Dacite	Diorite	Gabbro	Diorite	Diorite	Anddike	Rhyolite	Granod.	Granod.						
58.52	61.44	SiO2	57.79	58.12	57.29	56.19	57.75	57.23	57.55	64.79	61.33	50.41	55.57	60.66	60.48	78.57	66.15	67.68
0.86	0.66	TiO2	0.87	0.94	0.9	0.84	0.87	0.89	0.79	0.47	0.71	0.54	0.88	0.59	0.69	0.35	0.49	0.53
17.56	16.68	AI2O3	18.49	17.81	17.53	17.98	17.67	18.12	17.72	16.97	16.6	16.32	18.85	16.79	17.54	12.16	17.38	18.59
5.65	4.76	Fe2O3	6.42	6.4	6.32	6.56	6.34	6.47	6.36	2.87	5.52	6.89	7.6	4.91	4.67	1.28	3.13	1.79
0.11	0.09	MnO	0.11	0.11	0.1	0.13	0.08	0.12	0.12	0.05	0.08	0.12	0.14	0.12	0.08	0.02	0.04	0.02
3.1	2.49	MgO	3.41	3.76	3.77	3.48	3.55	3.87	3.41	1.22	2.88	5.13	3.96	2.22	3.86	0.4	1.19	0.46
6.1	4.46	CaO	6.6	6.81	6.58	6.4	6.38	7.02	6.34	3.88	4.92	17.23	7.57	5.46	2.55	0.02	2.52	0.85
3.69	3.86	Na2O	3.43	3.27	1.48	1.47	1.85	1.14	1.63	4.2	3.28	1.98	2.97	3.23	3.26	0.18	5.14	3.2
1.62	2.22	K2O	1.45	1.41	1.48	1.47	1.85	1.14	1.63	3.04	2.91	0.49	1.48	2.53	2.62	3.17	2.13	2.61
0.31	0.24	P2O5	0.35	0.3	0.3	0.33	0.31	0.29	0.29	0.21	0.21	0.09	0.27	0.39	0.29	0.05	0.21	0.18
1.58	1.81	LOI	1.05	1.17	1.22	1.59	1.71	1.25	2.04	1.21	0.69	0.59	-0.13	2.07	3.04	3.14	0.84	3.15
21.79	22.97	La	20.33	21.06	20.98	20.54	22.02	19.22	20.16	21.18	24.89	4.24	18.92	44.76	20.76	20.63	15.44	24.25
44.94	45.49	Ce	41.87	42.2	41.91	42.41	43.91	39.95	41.08	41.44	50.38	10.06	39.19	87.29	40.66	39.41	31.66	47.5
20.87	19.8	Nd	20.52	19.92	19.67	19.61	20.13	19.42	20	18.1	22.25	6.21	18.78	37.92	17.83	16.27	14.98	19.76
4.07	3.6	Sm	4.13	3.82	3.9	4.09	3.97	3.92	3.91	3.01	4.67	1.56	4.22	6.72	3.09	2.79	2.85	3.48
1.15	0.97	Eu	1.21	1.17	1.13	1.22	1.21	1.18	1.17	0.87	1.02	0.48	1.22	1.88	0.95	0.78	0.79	1.04
3.27	2.88	Gd	3.25	3.22	3.27	3.34	3.42	3.2	3.39	2.03	3.94	1.48	3.62	4.84	2.39	1.56	1.92	3.3
2.33	2.3	Dy	2.65	2.51	2.45	2.54	2.62	2.47	2.63	1.29	3.44	1.21	3.12	3.01	1.84	0.97	1.31	2.34
1.24	1.2	Er	1.36	1.23	1.18	1.46	1.38	1.31	1.42	0.55	1.91	0.65	1.67	1.47	0.91	0.49	0.69	1.01
1.06	1.14	Yb	1.29	1.05	1.13	1.46	1.27	1.19	1.35	0.53	1.86	0.68	1.64	1.35	0.96	0.49	0.59	0.86
14.28	14.12	Y	15.32	14.16	14.11	15.73	14.97	14.76	15.74	7.81	19.88	7.35	17.79	18.29	10.94	5.36	8.51	11.37
0.45	0.44	Ho	0.51	0.46	0.46	0.54	0.51	0.49	0.52	0.23	0.67	0.23	0.61	0.57	0.36	0.18	0.25	0.41
0.17	0.17	Lu	0.17	0.16	0.16	0.2	0.2	0.17	0.21	0.08	0.3	0.13	0.27	0.22	0.13	0.08	0.1	0.12
5.34	5.22	Pr	5.01	5	4.87	5.12	2.27	4.7	4.95	4.74	5.9	1.4	4.75	9.81	4.61	4.47	3.78	5.34
0.41	0.4	Tb	0.45	0.44	0.45	0.47	0.47	0.42	0.44	0.24	0.54	0.21	0.5	0.56	0.33	0.18	0.24	0.46
4.01	5.89	Th	2.72	3.93	3.83	3.28	4.3	2.64	4.18	3.62	11.55	0.83	3.63	9.31	5.84	3.68	3.72	6.12
0.78	1.3	U	0.63	1.03	0.96	0.66	0.99	0.55	1	1.57	2.92	0.34	0.91	2.82	1.91	1.15	0.73	2.57
0.964	0.921	Eu/Eu	1.01	1.02	0.967	1.009	1.004	1.019	0.982	1.076	0.727	0.966	0.954	1.008	1.069	1.143	1.032	0.938
14.745	14.45	La/Yb	11.304	14.39	13.318	10.091	12.437	11.585	10.712	28.665	9.599	4.473	8.275	23.782	15.512	31.2	18.771	20.226

Characteristics of Major, Rare Earth Elements, Sm-Nd, Rb-Sr, Oxygen, and Re-Os Compositions of Igneous Rocks

Abundances of Major and Rare Earth Elements

Eight samples of igneous rocks from the district plot in the calc-alkaline field and the other two plot in the tholeitic field (Fig. 44h). One of the two tholeitic samples is a Late Cretaceous-early Tertiary gabbro located in the southern part of the district, and the other is altered granodiorite from the Escondida deposit.

Paleozoic Felsic Rocks. The late Paleozoic rhyolite and andesite have a La/Yb ratio ranging from 6.6 to 10.13 with a moderate Eu negative anomaly that represents the most pronounced Eu anomaly among all the igneous rocks of the district (Fig. 44a). The REE pattern shows enrichment on light rare earth elements (LREE) and a relatively flat pattern for the medium rare earth elements (MREE) and heavy rare earth elements (HREE; Fig. 44a).

The Late Cretaceous Gabbros. The oldest igneous rock emplaced during the Late Cretaceous-Tertiary Andean magmatic cycle were gabbro that outcrop in the Cerro Bayo area, which is located 8 km south of the Escondida deposit (Marinovic et al., 1992; Richards et al., 2001; Fig. 4). These grabbros are the most mafic known igneous rocks in the district (44.4 % SiO₂; Table 8, and Fig. 46). The whole rock REE patterns of these gabbros show La/Yb ratios between 6 and 8 with a moderate Eu positive anomaly indicated by their Eu/Eu* ratios that vary between 1.1 and 1.5 (Table 8, Fig. 44b).

Late Paleocene-Early Eocene Volcanic Rocks. Sample "And" (Table 8) was collected approximately 14 km to the north of the Escondida deposit; it has been correlated with the Paleocene Augusta Victoria Formation (Perelló, 1984). A sample of a late Cretaceous andesite (70 Ma; Williams, 1992) from the Sierra Gorda district located



Fig. 44: REE normalized patterns and major oxides classification diagrams for igneous rocks from the Escondida district and other locations from northern Chile. Data after Rogers (1985), Marinovic et al. (1992), Richards and Boyce (2001), and this study.

approximately 150 km to the northeast of the Escondida district (Fig. 1) is included in this analysis to compare Paleocene andesite from Escondida with that from another locality (Table 8).

Figure 44b shows the REE patterns of the samples from the Escondida district and the Sierra Gorda district. Both REE patterns depict flat and similar levels of HREE; however, the REE patterns for the sample from Escondida shows an increase in LREE. This difference in LREE content is reflected by the La/Yb ratios, with a value of 10.8 for the Escondida andesite compared to a lower ratio of 4.05 for the sample from Sierra Gorda. Both samples have a similar weak-to-moderate Eu anomaly. The REE patterns from the Paleozoic rocks are similar to the patterns of the Paleocene andesite, but the negative Eu anomaly of the Paleozoic rocks is higher.

Eocene-Oligocene Igneous Rocks. In a QAP diagram presented in Figure 45, the most mafic Eocene-Oligocene igneous rocks from the Escondida district plot in the field of the quartz-monzodiorite but are locally known as diorite. The rocks associated with mineralization ("productive" intrusions) plot in the granodiorite field. Three samples plot in the quartz-rich granitoids field; they are samples "Rhy1-Esc4", "GdD-Esc3", and "LD-Esc6" (Table 8; Fig. 45). As indicated before, the three samples that plot in the quartz-rich granitoids field have LOI higher than 4% and are pervasively quartz-sericitized.

The granodiorite intrusions are mineralogically and chemically distinct from the diorite intrusions. The porphyritic granodiorite stocks have 2 to 8 volume percent igneous biotite and an almost complete absence of hornblende, whereas the diorites contain up to 30 volume percent of hornblende and nil biotite. The SiO₂ contents of



Fig. 45: QAP plot of igneous rocks from the Escondida district. QAP values were calculated using the norm of whole-rock analysis.



- △ Diorites from the central and eastern part of the district. 39 to 34 Ma, Richards, et al., 2000.
- Andesite porphyry (biotite-plagioclase) from Chimborazo, 38.09 ± 0.3 Richards et al., 2000.
- Dacite-Llamo porphyry from Zaldivar. Average age from the biotite grains 37.4 ± 0.18 Ma, and one age in a single grain of 36.28 ± 0.36 Ma. Richards et al., 2000.
- Granodiorite-porphyrytic intrusive rocks from Escondida Norte, this work.
- Phase 1 from the granodiorite-Escondida stock, ~38 Ma, this work.
- Phase 2 from the granodiorite-Escondida stock, ~38 Ma, this work.
- O Phase 3 from the granodiorite-Escondida Ssock, this work.
- * Post-mineralization rhyolite dome from the Escondida deposit, ~38 this work.
- + Post-mineralization rhyolite2 from the Escondida deposit, ~34 this work.
- Post-mineralization barren dikes from the Escondida deposit, ~34 Ma, this work.

Fig. 46: Plot of SiO2 and MgO concentrations for Late Eocene-Early Oligocene porphyritic intrusive rocks from the Escondida district. Non-italic numbers are La/Yb ratios as a measure of LREE/HREE fractionation. Italic numbers are Eu/Eu*, numbers higher than one reflect Eu enrichment, lower than one reflect Eu depletion.

granodiorite range from 65.6 to 69.7 volume percent and for diorites range from 57.8 to 62.82 volume percent (Fig. 46).

The REE patterns of the late Eocene-Oligocene igneous rocks differ from those of the older igneous rocks from the district. Their main difference with pre-Eocene igneous rocks is a lower MREE and HREE and the absence of a Eu anomaly, with Eu/Eu* ratios close 1.0 (Fig. 45).

There are small variations in the REE patterns within this group of late Eocene-Oligocene igneous rocks. The barren diorites and the productive granodiorites from the Escondida Norte and Chimborazo deposits have La/Ybratios that vary between 11.6 and 26.6, with a constant slope from La to Dy becoming shallower and slightly positive for the HREE elements (Dy to La). Their Eu/Eu* ratios are close to 1.0 (Fig. 44c). The "productive" granodiorite rocks from the Escondida and Zaldivar ore deposits show steeper REE profiles with lower MREE and HREE abundance, and La/Yb ratios that range from 19 to 31.2 (Fig. 44d). The granodioritic rocks from the Escondida deposit have Eu/Eu* ratios ranging from 0.86 to 1.14 (Fig. 44d). The REE patterns of the postmineral rhyodacitic rocks are similar to the pattern of granodiorites from the Escondida deposit.

Sm-Nd, Rb-Sr, and Oxygen Isotopes of Igneous Rocks

Sm-Nd and Rb-Sr isotope compositions were analyzed in the 10 samples from the Escondida district discussed in the previous paragraphs. No samples of barren dioritic rocks were analyzed (Table 9). The hydrothermal alteration probably does not affect the Nd isotope compositions (DePaolo, 1979), but it could have affected the Sr_o (⁸⁷Sr/⁸⁶Sr_{initial}) contents, resulting in more elevated values (Farmer and DePaolo, 1987).

Sample	Age (Ma)	Rx type	€ _{Nd(time)}	Sr _o	ref.	Formation-Location
CH 1-2	47.9	Gabbro	2.497420	0.703684	WCW	Paleocene Arc
SG 30-1	69.1	Andesite	2.650383	0.704513	WCW	Paleocene Arc
CC 1-1	73	Diorite	3.344506	0.704247	WCW	Paleocene Arc
SC 8-2	63	Diorite	2.574731	0.703888	WCW	Paleocene Arc
CC 16-3	62	Diorite	3.098705	0.705538	WCW	Paleocene Arc
SG 16-4	63	Quartz-diorite	2.564530	0.704252	WCW	Paleocene Arc
CH8-3	63	Quartz-diorite	2.490697	0.704519	WCW	Paleocene Arc
CC13-4	64	Quartz-diorite	2.791443	0.704388	WCW	Paleocene Arc
SG 19-1	60	Quartz-monzonite	2.918764	0.704947	WCW	Paleocene Arc
SG 1-1	63	Granodiorite	3.174753	0.704785	WCW	Paleocene Arc
SG 15-4	63	Granodiorite	2.082392	0.704892	WCW	Paleocene Arc
SC 7-3	70	Granodiorite	2.658250	0.704318	WCW	Paleocene Arc
CC 16-2	64	Granodiorite	1.706176	0.704507	WCW	Paleocene Arc
SB 6-3	64	Granodiorite	2.872798	0.704265	WCW	Paleocene Arc
CH 10-1	60	Granite	3.064534	0.704802	WCW	Paleocene Arc
CH 9-2	62	Rhyolite	2.998472	0.705170	WCW	Paleocene Arc
CC 6-2	63	Granite	1.060081	0.704603	WCW	Paleocene Arc
CC 13-1	58	Granodiorite	3.431305	0.704426	WCW	Paleocene Arc
8077	186	Andesite	5.775610	0.703470	RG	La Negra Fm.
8078	186	Andesite	4.916902	0.702920	RG	La Negra Fm.
8086	186	Andesite	3.941099	0.703300	RG	La Negra Fm.
8084	186	Andesite	6.653833	0.702960	RG	La Negra Fm.
8092	186	Andesite	6.380608	0.703180	RG	La Negra Fm.
8093	186	Andesite	5.151095	0.703200	RG	La Negra Fm.
8097	186	Andesite	5.717062	0.703010	RG	La Negra Fm.
8098	186	Andesite	5.873190	0.703040	RG	La Negra Fm.
81114	265	Granodiorite	-1.326913	0.706230	RG	Limo Verde Pluton
81118	265	Granodiorite	-1.385473	0.706030	RG	Limo Verde Pluton
81119	265	Granodiorite	-1.990590	0.706490	RG	Limo Verde Pluton
81121	265	Granodiorite	-2.459069	0.705720	RG	Limo Verde Pluton
81041	233	Rhyolite	-2.470537	0.706550	RG	Co. Crespo Fm.
81042	233	Rhyolite	-0.850514	0.707570	RG	Co. Crespo Fm.
81045	233	Rhyolite	-1.963060	0.708310	RG	Co. Crespo Fm.

Table 9. Sm-Nd and Rb-Sr isotopic data from igneous rocks of northern Chile. WCW from Williams (1992);RG from Rogers (1989); and the ten samples in bold are from this study.

Sample	Age (Ma)	Rx type	$\boldsymbol{\epsilon}_{Nd(time)}$	Sr _o	ref.	Formation-Location
80103	39	Granodiorite	1.848761	0.704510	RG	El Abra Deposit
80104	39	Granodiorite	1.380549	0.704570	RG	El Abra Deposit
80107	39	Granodiorite	1.458585	0.704470	RG	El Abra Deposit
Esc10	265	Rhyolite	-1.481897	0.708243	This study	Rhyolite
And	60	Andesite	1.894500	0.704802	This study	Host rock Escondida
EscN1	38	Granodiorite	0.387172	0.704510	This study	Esc. Norte Deposit
EscN2	38	Granodiorite	0.218005	0.704570	This study	Esc. Norte Deposit
Esc1	38	Granodiorite	0.633494	0.704470	This study	Esc. Deposit
Esc2	38	Granodiorite	0.767460	0.704510	This study	Esc. Deposit
Esc3	38	Granodiorite	0.169687	0.704570	This study	Esc. Deposit
Esc4	38	Rhyolite	0.315532	0.705000	This study	Esc. Deposit
Esc5	35	Rhyolite	-0.046301	0.704800	This study	Esc. Deposit
Esc6	34	Rhyolite	0.042914	0.704700	This study	Esc. Deposit

 Table 9. Continued.

Table 10. Re-Os Data

Location	Mineral	Os (ppt)	Re (ppt)	¹⁸⁷ Os/ ¹⁸⁸ Os	¹⁸⁷ Re/ ¹⁸⁸ Os	(¹⁸⁷ Os/ ¹⁸⁸ Os) _i	Age (Ma)
Esc1	magnetite	12	2022	1.390670	1136.71	0.67	38
Esc2	magnetite	61	41337	4.802670	5316	1.45	38
Esc8	magnetite	20	2589	0.716000	677	0.29	38
Esc31	molybdenite		1355ppm				33.7+/-0.3

Concentrations, isotopic ratios, initial ratios, and ages (from U-Pb and Ar-Ar data) of magnetites from the first two "productive" granodioties and a magnetite sample from an early biotite-orthoclase vein.



Fig. 47: ENdt versus Sr₀ for Permian to Oligocene rocks from the Escondida district (this work). Also included are values from other arcs of northern Chile (after Rogers, 1985, and Williams, 1992).

The "productive" and post-mineral Eocene-Oligocene igneous rocks are not distinguished by the Sm-Nd and the Rb-Sr isotopic data. The granodioritic and rhyodacitic rocks from Escondida and Escondida Norte deposits form a tight group between 0 and 1 $C_{Nd(time)}$ and Sr_o (initial Sr ratio) values that range between 0.704953 and 0.705867(Fig. 47).

The andesite from Escondida has a $C_{Nd(time)}$ close to 2, which is similar to the value of Paleocene andesite from other parts of northern Chile (Fig. 47). The $C_{Nd(time)}$ of the Paleozoic rhyolite presents the lowest value of all the analyzed samples (–1.8 in Fig. 47) and has a very large Sr_o (0.710). End member $C_{Nd(time)}$ and Sr_o values used in the calculation of the mixing curve presented in Figure 48 are the a Paleozoic rhyolite (basement) analyzed by Williams (1992) and a Jurassic volcanic rock sample of the La Negra Formation (Rogers, 1985).

¹⁸⁷Os/¹⁸⁸Os Isotopic Compositions of Magnetite

The Re-Os analysis of sulfides from the Escondida and Escondida Norte deposits did not produce reliable data owing to their high Re contents, which may reflect supergene effects or the presence of small inclusions of molybdenite (Mathur, 2000). To overcome this problem, Re-Os data were obtained from three samples of magnetite from the Escondida deposit that yielded ¹⁸⁷Os/¹⁸⁸Os ratios between 0.28 and 1.44 (Table 10). Two samples of igneous magnetite were separated from the first two intrusive phases of the Escondida stock (samples "D71mt"=Esc1 and "RD1416mt"=Esc2), and one hydrothermal sample was separated from a thick biotite-anhydrite-magnetite-chalcopyrite-bornite vein (sample "D17Bt"=Esc1Bt). The ¹⁸⁷Os/¹⁸⁸Os ratio of magnetite from the crowded first intrusive phase of the Escondida stock yielded the higher

 187 Os/ 188 Os ratio of 1.44, while the magnetite from the second intrusive phase of the Escondida stock gave the lowest or less radiogenic 187 Os/ 188 Os ratio of 0.28. The 187 Os/ 188 Os ratio of the hydrothermal magnetite yielded an intermediate value of 0.67.

Correspondence of Magmas with Sm-Nd, Rb-Sr, and Oxygen Isotopic Compositions

The relative proportions of mantle and crustal components can be evaluated reviewing the Sm-Nd, Rb-Sr, and oxygen isotopic compositions. The δ^{18} O isotopic values, calculated at 700 °C, from the Eocene-Oligocene igneous rocks from the Escondida deposit range between 7.2 and 8.2 per mil (Table 7), suggesting a mantle source or that they were derived from an igneous parent (Taylor, 1978).

The $C_{Nd(time)}$ and Sr_o values of rocks from Escondida presented above suggest a magma source associated with an enriched or an undepleted mantle or with a crustal source that crystallized from mantle material a few million years before being remelted (Fig.47).

Interpretation of ¹⁸⁷Os/¹⁸⁸Os Initial Values of Magnetites

An interpretation of the limited Re-Os data from the Escondida deposit has been suggested by Mathur (2000). Mathur (2000) postulates that the hydrothermal magnetite could have formed as a mixture of two granodioritic magmatic events of the Colorado Grande (D71=Esc1mt) and Escondida (RD1246=Esc2mt) intrusive phases. Mathur's interpretation suggests that most of the Re-Os was supplied from non-radiogenic material that may have originated in the mantle or in rocks of the crust that have not had time to decay to more radiogenic compositions. These optional sources will be discussed in the last section of this chapter.

			I		II										IV		
Steps		Partial	Melting	Mix-A	ssimilat	tion	1		C	ryst	alliza	ation	1		Mix-Assin	nilatio	n 2
		%	%	%	%	%		%	%	%	%	%	%	%	%	%	%
Models		SpLerz	GnLerz	SpLerz	GnLerz	LC	Sh	ol	grn	plg	срх	орх	hb	F	Melt	UC	Sh
	1	6	2	65	35			60				20	20	40			
	2	2	2	50	50												
	3		5		60	40		60				20	20	20			
	4	5	1	50	40	10											
	5	Good matc	h is reache	d by dire	ct partial	meli	ting o	of sp	inel	man	tle						

Table 11. REE models of gabbros of the Escondida region.

SpLerz = spinel-stable lithospheric mantle; **GnLerz** = garnet-stable mantle; **Granulite** = lower crust stable in the granulite metamorphic facies of mafic composition; **LC** = mafic upper crust in amphibolite metamorphic facies; **UC** = upper crust of felsic composition; **Sh** = shales. **Ol** = olivine; **grn** = garnet; **plg** = plagioclase; **opx** = orthopyroxene; **cpx** = clinopyroxene; **hb** = hornblende. **F%** = the percent of the melt that is left behind in a crystallized residue.

Binary mixing and partial melting equations (Rollinson, 1993; Appendix E). Partitioning coefficients from Arth (1976);

Green and Pearson (1985); Dostal et al. (1983); Fujimaki and Hildreth (1983). Mantle and lower crust composition

from Rudnick and Fountain (1995). Mantle mineralogy from Philpotts (1989). Shale composition from Taylor and McLennan (1995). Upper felsic crust composition from Williams (1992).

					II										IV		
Steps		Partial	Melting	Mix-A	ssimilat	tion	1		C	ryst	alliza	ation	1		Mix-Assin	nilatio	n 2
		%	%	%	%	%		%	%	%	%	%	%	%	%	%	%
Models		SpLerz	GnLerz	SpLerz	GnLerz	LC	Sh	ol	grn	plg	срх	орх	hb	F	Melt	UC	Sh
	1	3	2	55	40	5	0	0	0	0	0	0	0	0			
		A good match	with the ande	site from E	scondida												
	2	10	2	20	60	20	0	20		40	0	20	20	70	95	5	
		A good match	with the ande	site from E	scondida												
	3	10	1	30	60	10	0	40		40		10	20	52	80	10	10
		A good match	with the ande	site from E	scondida												
	4	10	0	100	0	0	0	20				20	20	60	85	10	5
		A perfect mat	ch with the an	desite from	Williams												
	5	10	10	60	20	20	0	20		40		20	20	45	70	20	10
		Perfect match	with the REE	pattern fro	m Williams	, but	Esc h	as hi	gher H	IREE	value	s					
	6		7to8		70	25	5	80		40		20	0	45	50	50	
	7	A good match	using and init	ial melt eq	ual to the g	abbro	o. The	en cry	stalliz	ing ar	nd ass	imilati	ng up	per fel	sic crust,		
		5% of shales	from the lower	or upper c	rust can be	e inclu	uded a	and th	ne RE	E pat	tern do	oes no	t cha	nge si	gnificantly.		

Table 12. REE models of Paleocene andesites of the Augusta Victoria Formation.

SpLerz = spinel-stable lithospheric mantle; **GnLerz** = garnet-stable mantle; **Granulite** = lower crust stable in the granulite metamorphic facies of mafic composition; **LC** = mafic upper crust in amphibolite metamorphic facies; **UC** = upper crust of felsic composition; **Sh** = shales. **Ol** = olivine; **grn** = garnet; **plg** = plagioclase; **opx** = orthopyroxene; **cpx** = clinopyroxene; **hb** = hornblende. **F%** = the percent of the melt that is left behind in a crystallized residue.

Binary mixing and partial melting equations (Rollinson, 1993; Appendix E). Partitioning coefficients from Arth (1976); Green and Pearson (1985); Dostal et al. (1983); Fujimaki and Hildreth (1983). Mantle and lower crust composition from Rudnick and Fountain (1995). Mantle mineralogy from Philpotts (1989). Shale composition from Taylor and McLennan (1995). Upper felsic crust composition from Williams (1992).

														IV			VI		
Steps	Pa	artial Mel [.]	ting	Mi	x-Assim	ilation 1		С	rysta	alliza	ation	1		Mix-Assir	milation 2	Cr	ystalli	zatio	n 2
	%	%	%	%	%	% %	%	%	%	%	%	%	%	%	% %	%	%	%	%
Models	SpLerz	GnLerz	Granulite	SpLerz	GnLerz	Granulite L0) ol	grn	plg	срх	орх	hb	F	Melt	UC Sh	ol	plg	hb	F
	With "no"	participatio	on of garnet-	stable low	er crust (g	ranulite metam	orphic	phas	e)										
1	1	1		10	90		30		40			30	65	90	10				
	An exceller	nt match wit	h the steepes	t line patte	rn of diorite	es													
2	1	1			90	1() 30		40			30	60	75	15 10				
	An exceller	nt match wit	h the least-ste	eep line pa	ttern of the	diorites													
3	10	1		10	90		30		40			30	60	90	10				
	An exceller	nt match wit	h REE patteri	n of granoc	liorites fron	n Escondida Nor	te												
4	10	1			90	1() 30		40			30	60	95	5				
	An exceller	nt match wit	h the REE pa	ttern of the	phase one	e granodiorite of	the Es	condid	a stoc	k									
5	10	1			90	1() 30		40			30	30	95	5				
	With partic	cipation of	garnet-stable	e lower cru	ust (granu	lite metamorphi	c pha	se)											
6	10	10	1	10	10	80	50	5		15	30		30	90	10		60	40	50
	A very good	d match wit	h the second	intrusive pl	hase of the	Escondida stoc	(
7	10	10	1	10	40	50	50			15	30	5	30	70	30		60	40	20
	A very good	d match wit	h the second	intrusive pl	hase of the	Escondida stoc	(
8	10	10	1	10	10	80 10) 50			15	30	5	30	90	10		60	40	20
	A good mat	tch with dor	ites and some	e of the gra	nodiorites	of the Escondida	distric	t											
9	10	10	1	10	30	40 20) 50			15	30	5	30	80	20		60	40	10
	A good mat	tch with dor	ites of the Es	condida dis	strict														

Table 13. REE models of diorites and granodiorites of the Escondida region.

SpLerz = spinel-stable lithospheric mantle; **GnLerz** = garnet-stable mantle; **Granulite** = lower crust stable in the granulite metamorphic

facies of mafic composition; LC = mafic upper crust in amphibolite metamorphic facies; UC = upper crust of felsic composition;

Sh = shales. Ol = olivine; grn = garnet; plg = plagioclase; opx = orthopyroxene; cpx = clinopyroxene; hb = hornblende.

F% = the percent of the melt that is left behind in a crystallized residue.

Binary mixing and partial melting equations (Rollinson, 1993; Appendix E). Partitioning coefficients from Arth (1976);

Green and Pearson (1985); Dostal et al. (1983); Fujimaki and Hildreth (1983). Mantle and lower crust composition

from Rudnick and Fountain (1995). Mantle mineralogy from Philpotts (1989). Shale composition from Taylor and McLennan (1995).

Upper felsic crust composition from Williams (1992).

Calculated REE Patterns

The calculated patterns from partial melting assimilation-crystallization models that reproduce the REE patterns of the Late Cretaceous-Oligocene igneous rocks of the Escondida district are presented in Tables 11, 12, and 13. The selected calculated models are constrained by the Sm-Nd and the Rb-Sr data, which indicate a major radiogenic component in all the Tertiary rocks of the Escondida district.

REE Patterns from Samples of the Late Cretaceous Gabbros

The REE patterns of the Late Cretaceous gabbro can be reproduced by direct partial melting of spinel-stable upper mantle or by mixing of a partial melt from a garnetstable mantle source with partial melt from the spinel-stable mantle source (Table 11). Minor amounts of crustal assimilation and less than 10 volume percent crystallization (olivine-orthopyroxene-hornblende) can be taken into account without a major effect on the final shape of the REE patterns of the gabbro (Table 11).

REE Patterns of the Paleocene Andesite

The pattern presented by the LREE elements of the Paleocene andesite sample from the Escondida district (Fig. 44) can be calculated by the magma mix formed by less than 10 percent partial melting of garnet and spinel-stable peridotite with an assimilation of less than 20 volume percent mafic lower and upper garnet-absent crustal material (Table 12).

REE Patterns of the Late Eocene-Oligocene Igneous Rocks

The REE patterns of the Late Eocene-Oligocene igneous rocks can be calculated as follows: 1) mixing of a large volume of a magma formed by less than 10 percent partial melting of garnet-stable lithospheric mantle with less than 20 volume percent of magma

produced by assimilation of a garnet-absent crust (Table 13), and 2) mixing of more than 75 volume percent of magma generated by 1 percent partial melting of garnet-stable lower crust with less than 20 percent of magma formed by less than 10 percent partial melting of lithospheric mantle and minor amounts of assimilation of a garnet-absent crust (Table 13).

Interpretation and Discussion

The Escondida porphyry copper system was developed at the end of a 12 Ma calc-alkaline magmatic event, with Sm/Nd and Rb/Sr isotope values that indicate a dominant mantle component for its associated igneous rocks. The late Eocene-Oligocene igneous rocks from Escondida have steep REE patterns, which is a feature also associated with other porphyry copper districts of northern Chile, including Chiquicamata (Maksaev, 1990) and El Salvador (Cornejo et al., 1997).

The steep REE patterns could be explained by the three following possibilities:

- 1. Low partial melting in a garnet-stable source rock.
- 2. Contamination of LREE from the melting of subducted sediments.
- 3. Anomalous composition of the lithospheric mantle along the axis of the large porphyry copper belt of northern Chile.

The first possibility is investigated by the models calculated in this dissertation (Table 13). Reasonable garnet-containing sources are the deep lithospheric mantle or the bottom of a 60 km or thicker crust. The present thickness of the crust at the Escondida region is approximately 57 km (Jürgen et al., 1994), and the region has been tectonically quiescent since the formation of the porphyry systems; therefore, the crustal thickness when the porphyries were developed was probably close to 60 km. A suggested

shortening of the crust in the Escondida region of at least 25 percent from the Paleocene to the Eocene (Scheuber et al., 1994) allows an estimation of crustal thickness for the Paleocene of approximately 40 km, with a bottom of the crust in the amphibolite-stable region (Fig. 48). Therefore, the late Cretaceous-Paleocene gabbros and andesites were probably emplaced in a crust no thicker than 45 km, with an amphibolite-stable lower crust (Fig. 48), whereas the late Eocene-Oligocene magmas were formed by melting in a thick crust within a garnet-stable zone (Fig. 49).

The second possibility has been used to explain steep REE patterns of igneous rocks from the Lesser Antilles, where the contamination from continental crust is low because of the thickness and basaltic composition of the crust in that part of the world (Davidson, 1987). However, consideration of this possibility becomes more complicated where magma has interacted with thick continental crust. If this were a valid mechanism for the formation of the late Eocene-Oligocene magmatic arc of northern Chile, the high copper contents could come from the melting of clay material that contains high background values of copper.

The third possibility was proposed by Rogers (1985) after a detailed geochemical study along a cross section of the Andes of northern Chile, at the latitude of Chuquicamata. There are no more studies supporting this idea, and the data of this study do not allow further consideration.

Copper resources increase from the Mesozoic to the late Eocene-Oligocene arcs of northern Chile (Sillitoe, 1988). The igneous rocks of the Mesozoic arc present the lowest LREE contents, whereas the late Eocene-Oligocene intrusions present the highest LREE patterns (Fig. 44f). The $C_{Nd(time)}$ numbers become less negative and closer to zero

from the Mezosoic to the Late Eocene-Oligocene (Fig. 47). The correlation between high LREE and large copper budgets has also been observed in the Laramide porphyry copper systems of Arizona (Anthony and Titley, 1988; Lang and Titley, 1998). Despite the compositional observation of igneous rocks indicated in this chapter, there is no clear genetic correlation between sources of magmas, the enrichment of LREE, and the large copper budgets in porphyry copper deposits.



Fig. 48: Schematic east-west section, looking south, including the possible structure and main components of the crust of the western margin of northern Chile during the Paleocene. Metamorphic facies from Philpotts (1989), isotherms from Davies and Stevenson (1992), age of the magmatic arcs from this work.



Fig. 49: Schematic east-west section, looking south, of the possible structure and main components of the crust of the western margin of northern Chile during the Late Eocene-Oligocene. Metamorphic facies from Philpotts (1989), isotherms from Davies and Stevenson (1992), age of the magmatic arcs from this work.

CHAPTER 7

INTERPRETATION OF THE EVOLUTION OF THE ESCONDIDA DEPOSIT

In this section I will give my preferred interpretation of the evolution of the Escondida porphyry deposit based on data presented, interpreted, and discussed previously in this thesis.

The Sm-Nd and Rb-Sr data indicate that the Escondida stock was formed from magmas of dominantly mantle origin and from lower crustal material of short residence before melting in the late Eocene-Oligocene. The crustal thickness in the Escondida region during the Late Eocene-Oligocene was about 60 km, making the lower crust garnet stable, which is reflected in the steep REE patterns of the late Eocene-Oligocene igneous rocks.

At the Escondida district, a magnetic anomaly is co-spatial with outcrops of quartz diorite that may indicate the batholith from which the more differentiated magmas and their associated hydrothermal phases intruded along an extensional zone of the Domeyko Fault System at approximately 38 Ma (Fig. 50). The opening of the main NNW-striking shear zones of the Domeyko Fault System facilitated the upward movement of the buoyant granodioritic magma, and the N40°W orientation of the extensional gash controlled the final orientation of the Escondida granodioritic stock (Fig. 11). About 3 km depth the cooling granodioritic magma crystallized with a consequent release of energy that resulted in fracturing of the crystallized intrusion and the host rock and in the segregation of fluids, as described by Burnham (1979) for shallow emplacement of granodioritic magmas. The potassic hydrothermal alteration mineral assemblage formed during the unmixing of magmatic fluids with temperature ranging from 400 ° to 550 °C. The active transtensional structural regime diminished the escape of the low density fluid produced during the formation of the potassic event. This low density fluid unmixed below 400 °C forming the copper bearing quartz-sericitic mineral assemblage that later mixed with meteoric waters at the lower temperatures of this event.

The granodioritic stock and its associated two early mineralizing events were cut by rhyolite dikes and two advanced argillic events at approximately 36 and 34 Ma, respectively. The waters associated with the advanced argillic events represent a progression toward meteoric composition as temperatures fall from 300° to below 200°C. Sulfur isotope values from sulfides plot close to zero differentiating three population; values of the potassic event with the lowest δ^{34} S numbers, values of the sericitic event with δ^{34} S numbers close to zero, and a population with the larger distribution range of δ^{34} S values that represent samples from the advanced argillic events. The sulfur isotope data indicate magmatic origin for sulfur and suggest that part of advanced argillic sulfide phase could have formed by leaching sulfides of the two earlier mineralizing events. The extent of the possible leaching and enrichment generated by acid fluids of the advanced argillic events has not been fully evaluated in this study but possibly contributed to the formation of one the richest and largest accumulation of chalcocite-covellite mineralization in the world.

The overprinting of magmatic and hydrothermal events seems to have been a key factor in the formation of the giant Escondida porphyry copper deposit that was later

enriched during the changing climatic conditions of the Atacama desert and preserved by low rates of denudation that followed the emplacement of the porphyry system.





<u>APPENI</u>	DIX A.	SAMPLE LOC	ATIONS									
Sample	Other Code	Location	E-W	N-S	$\delta^{18}O\ \%$	δD‰	δS‰	Ar-Ar	U-Pb	Re-Os	Geoch	Sm-Nd
Esc00	PzRhy	Outcrop	E16494	N107332							х	х
Esc1	D71-450m	D71-450m	E15746	N108177	х	х		х	х	х	х	х
Esc2	D1343-300m	D1343-300m	E15800	N108225	х	х		х	х	х	х	х
Esc3		Pit	E15000	N108601							х	х
Esc4	Rhy1	RD-937-250m	E16450	N108600	х	х			х		х	х
Esc5	Rhy2	Pit-East Wall	E17400	N108000	х			х			х	х
Esc6	LateDike-LD	Pit-North Wall	E17100	N107000	х				х		х	х
Esc7	DHH353-97m	D353-97m	E15450	N107478	х	х	х	х				
Esc8	D17(350m)	D17(350m)	E16068	N107638	x	х	х	х		х		
Esc9	K-Vein2	D258-891	E15900	N107400	х	х	х	х				
Esc10	K-Vein3	D27-210m	E16650	N107376			х					
Esc11		D52(320m)	E14951	N108778	x							
Esc12		D1141(520m)	E15612	N107645	х							
Esc13		2700bench	E16165	N108179	x							
Esc14	GS2	Pit-West Wall	E16580	N107650	х	х	х	х				
Esc15	GS3	Pit-West Wall	E16580	N108100	х	х	х	х				
Esc16	GS4	Pit-West Wall	E16029	N108365	x	х	х					
Esc17	GS5	D1460-130m	E15800	N108225	x	х	х					
Esc18	WS1	D1452-300m	E15611	N107645	x	х	х	х				
Esc19	WS2	D1463-120	E16451	N107478	x	х	х	х				
Esc20	WS3	D1440-300m	E16461	N108635	x	х	х					
Esc21	WS4	D1440-300m	E16461	N108635	x	х	х					
Esc22		D1115(180m)	E16380	N107732	x	х	х					
Esc23		D1115(257m)	E16380	N107732	x	х	х					
Esc24	Illite1	Pit	E14803	N108798	x	х	х	х				
Esc25	Illite2	Pit	E16050	N107100	x	х	х					
Esc26	Rhv1	Pit	E15770	N108132			х	х				
Esc27	Alun2	Pit-North Wall	E16450	N108600			x	x				
Esc28	Alun3	D1105(257m)	F16088	N107794			x					
Esc29	Alun4	D1105(300m)	E16088	N107794			x					
Esc30	And1	Outcrop	E16493	N107335							x	x
Esc31	Mo1	Pit-Fast wall	E17000	N107600						x	~	
Zal1	7al1	Tunnel	E16494	N107322						~	x	x
7al2	Zal2	DDH	E16495	N107321							x	x
	2012		_ 10 100								~	^

APPENDIX A. SAMPLE LOCATIONS

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APPENDIX B

Ar-Ar GEOCHRONOLOGY – LABORATORY DESCRIPTION AND PROCEDURES

Samples analyzed by the 40 Ar/ 39 Ar method at the University of Nevada, Las Vegas, were wrapped in Al foil and stacked in 6 mm inside diameter Pyrex tube. Individual packets averaged 3 mm thick, and neutron fluence monitors (ANU 92-176, Fish Canyon Tuff sanidine) were placed every 5-10 mm along the tube. Synthetic K-glass and optical grade CaF₂ were included in the irradiation packages to monitor neutroninduced argon interferences from K and Ca. Loaded tubes were packed in an Al container for irradiation. Samples were irradiated for 14 hours in the D3 position on the core edge (fuel rods on three sides, moderator on the fourth side) of the 1MW TRIGA type reactor at the Nuclear Science Center at Texas A&M University. Irradiations are performed in a dry tube device, shielded against thermal neutrons by a 5 mm thick jacket of B₄C powder, which rotates about its axis at a rate of 0.7 revolutions per minute to mitigate horizontal flux gradients. Correction factors for interfering neutron reactions on K and Ca were determined by repeated analysis of K-glass and CaF₂ fragments. Measured $({}^{40}\text{Ar}/{}^{39}\text{Ar})_{\text{K}}$ values were 1.38 (±0.30) x 10⁻². Ca correction factors were $({}^{36}\text{Ar}/{}^{37}\text{Ar})\text{Ca} = 2.78 (\pm 0.02) \times 10^{-4} \text{ and } ({}^{39}\text{Ar}/{}^{37}\text{Ar})\text{Ca} = 6.82 (\pm 0.11) \times 10^{-4}$. J factors were determined by fusion of 4-5 individual crystals of neutron fluence monitors, which gave reproducibilities of 0.05% to 0.27% at each standard position. Variation in neutron flux along the 100 mm length of the irradiation tubes was <4%. An error in J of 0.5% was used in age calculations. No significant neutron flux gradients were present within

individual packets of crystals as indicated by the excellent reproducibility of the single crystal flux monitor fusions.

Irradiated crystals together with CaF₂ and K-glass fragments were placed in a Cu sample tray in an high vacuum extraction line and were fused using a 20 W CO₂ laser. Sample viewing during laser fusion was by a video camera system and positioning was via a motorized sample stage. Samples analyzed by the furnace step heating method utilized a double vacuum resistance furnace similar to the Staudacher et al. (1978) design. Reactive gases were removed by a single MAP and two GP-50 SAES getters prior to being admitted to a MAP 215-50 mass spectrometer by expansion. The relative volumes of the extraction line and mass spectrometer allow 80 percent of the gas to be admitted to the mass spectrometer for laser fusion analyses and 76 percent for furnace heating analyses. Peak intensities were measured using a Balzers electron multiplier by peak hopping through 7 cycles; initial peak heights were determined by linear regression to the time of gas admission. Mass spectrometer discrimination and sensitivity was monitored by repeated analysis of atmospheric argon aliquots from an on-line pipette system. Measured ${}^{40}\text{Ar}/{}^{36}\text{Ar}$ ratios were 289.79 + 0.35% during this work, thus a discrimination correction of 1.01971 (4 AMU) was applied to measured isotope ratios. The sensitivity of the mass spectrometer was $\sim 2 \times 10^{-17}$ mol mV⁻¹ with the multiplier operated at a gain of 100 over the Faraday. Line blanks averaged 1.8×10^{-16} mol for mass 40 and 8.0 x 10^{-19} mol for mass 36 for laser fusion analyses and 7.0 x 10^{-16} mol for mass 40 and 2.6 x 10⁻¹⁸ mol for mass 36 for furnace heating analyses. Discrimination, sensitivity, and blanks were relatively constant over the period of data collection. Computer automated operation of the sample stage, laser, extraction line, and mass

spectrometer, as well as final data reduction and age calculations, were done using LabVIEW software written by B. Idleman (Lehigh University). An age of 27.9 Ma (Steven et al., 1967; Cebula et al., 1986) was used for the Fish Canyon Tuff sanidine flux monitor in calculating ages for samples.

For ⁴⁰Ar/³⁹Ar analyses, a plateau segment consists of three or more contiguous gas fractions having analytically indistinguishable ages (i.e., all plateau steps overlap in age at $\pm 2_{\sigma}$ analytical error) and comprising a significant portion of the total gas released (typically >50%). Total gas (integrated) ages are calculated by weighting by the amount of ³⁹Ar released, whereas plateau ages are weighted by the inverse of the variance. For each sample, inverse isochron diagrams are examined to check for the effects of excess argon. Reliable isochrons are based on the MSWD criteria of Wendt and Carl (1991) and, as for plateaus, must comprise contiguous steps and a significant fraction of the total gas released. All analytical data are reported at the confidence level of 1_{σ} (standard deviation).

APPENDIX C.	Ar-Ar ISOTOPIC	C DATA AND AGES
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Esc7Bt, biotite (Pervasive Biotite)	. 13.36 ma. J = 0.001598+/- 0.5%

step	T (C)	t (min.)	36Ar	37Ar	38Ar	39Ar	40Ar	%40Ar*	% 39Ar rlsd	Ca/K	40Ar*/39ArK	Age (Ma)	1s.d.
1	550	12	41.019	3.853	8.222	16.897	13847.3	14.2	1.40968097	0.84513915	116.908732	308.998	10.165
2	580	12	18.185	4.051	3.846	19.239	5783.577	9	1.60506908	0.78038715	27.0053223	76.221	1.03
3	620	12	18.819	3.634	4.26	31.321	6362.427	9.8	2.61304478	0.42996578	19.959874	56.644	0.809
4	660	12	12.492	3.671	2.968	43.695	4334.308	16.8	3.64538143	0.31133054	16.4751506	46.882	0.422
5	700	12	9.141	5.297	2.667	71.773	3692.44	28.4	5.98786959	0.27348469	14.6290838	41.689	0.277
6	750	12	6.368	6.586	2.834	118.279	3427.278	46.4	9.8677668	0.20633336	13.4417129	38.341	0.23
7	800	12	5.258	4.897	2.339	101.108	2873.524	47.3	8.43522659	0.17947189	13.4183281	38.275	0.228
8	850	12	5.335	4.286	2.159	80.36	2674.711	42.5	6.70426483	0.19763619	14.1230824	40.263	0.248
9	900	12	3.83	4.178	1.804	81.472	2240.246	50.9	6.79703664	0.19002612	13.9489486	39.772	0.236
10	945	12	2.891	6.393	1.443	64.188	1717.189	51.9	5.35506908	0.36908593	13.7865611	39.314	0.243
11	985	12	3.034	6.718	1.443	65.089	1772.006	51	5.4302376	0.38248181	13.8028689	39.36	0.238
12	1030	12	2.848	10.204	2.025	112.095	2347.505	65.4	9.35184876	0.33733134	13.6511514	38.932	0.224
13	1070	12	2.33	11.562	2.578	157.627	2722.142	76	13.1504872	0.27181053	13.1027169	37.384	0.213
14	1115	12	2.023	13.158	2.395	149.615	2490.211	77	12.482063	0.32590103	12.7773507	36.465	0.208
15	1155	12	1.507	15.173	1.207	66.648	1284.36	67.1	5.56030168	0.84376785	12.790801	36.503	0.221
16	1400	12	1.305	18.538	0.498	19.236	626.101	42.1	1.60481879	3.57473048	13.3173581	37.99	0.287
						Cumulative	e %39Ar risc	=	100.000167	no plateau	Total gas age	43.66997	0.20629
Esc8	Bt. biot	ite (Vein	-Pervasiv	ve Biotite). 11.02	ma. J = 0.	0015925+/-	0.5%					
	.,				<i>p</i>	J,							
step	T (C)	t (min.)	36Ar	37Ar	38Ar	39Ar	40Ar	%40Ar*	% 39Ar rlsd	Ca/K	40Ar*/39ArK	Age (Ma)	1s.d.
step 1	T (C) 525	t (min.) 12	36Ar 6.045	37Ar 0.978	38Ar 1.182	39Ar 3.096	40Ar 1837.198	%40Ar* 4.7	% 39Ar rlsd 0.17488601	Ca/K 1.15032862	40Ar*/39ArK 27.8698837	Age (Ma) 78.344	1s.d. 3.886
step 1 2	T (C) 525 565	t (min.) 12 12	36Ar 6.045 3.312	37Ar 0.978 0.846	38Ar 1.182 0.75	39Ar 3.096 7.089	40Ar 1837.198 1006.842	%40Ar* 4.7 4.9	% 39Ar rlsd 0.17488601 0.40044151	Ca/K 1.15032862 0.43448612	40Ar*/39ArK 27.8698837 6.797421	Age (Ma) 78.344 19.424	1s.d. 3.886 1.028
step 1 2 3	T (C) 525 565 605	t (min.) 12 12 12 12	36Ar 6.045 3.312 6.025	37Ar 0.978 0.846 1.69	38Ar 1.182 0.75 1.421	39Ar 3.096 7.089 19.415	40Ar 1837.198 1006.842 1842.657	%40Ar* 4.7 4.9 5.3	% 39Ar rlsd 0.17488601 0.40044151 1.09670925	Ca/K 1.15032862 0.43448612 0.31690163	40Ar*/39ArK 27.8698837 6.797421 5.011902	Age (Ma) 78.344 19.424 14.342	1s.d. 3.886 1.028 0.673
step 1 2 3 4	T (C) 525 565 605 645	t (min.) 12 12 12 12 12	36Ar 6.045 3.312 6.025 5.63	37Ar 0.978 0.846 1.69 2.035	38Ar 1.182 0.75 1.421 1.391	39Ar 3.096 7.089 19.415 21.828	40Ar 1837.198 1006.842 1842.657 1849.57	%40Ar* 4.7 4.9 5.3 11.9	% 39Ar rlsd 0.17488601 0.40044151 1.09670925 1.23301414	Ca/K 1.15032862 0.43448612 0.31690163 0.33941308	40Ar*/39ArK 27.8698837 6.797421 5.011902 10.0192482	Age (Ma) 78.344 19.424 14.342 28.558	1s.d. 3.886 1.028 0.673 0.59
step 1 2 3 4 5	T (C) 525 565 605 645 700	t (min.) 12 12 12 12 12 12 12	36Ar 6.045 3.312 6.025 5.63 5.458	37Ar 0.978 0.846 1.69 2.035 2.593	38Ar 1.182 0.75 1.421 1.391 1.719	39Ar 3.096 7.089 19.415 21.828 50.476	40Ar 1837.198 1006.842 1842.657 1849.57 2231.325	%40Ar* 4.7 4.9 5.3 11.9 29.4	% 39Ar rlsd 0.17488601 0.40044151 1.09670925 1.23301414 2.85127459	Ca/K 1.15032862 0.43448612 0.31690163 0.33941308 0.18701471	40Ar*/39ArK 27.8698837 6.797421 5.011902 10.0192482 12.9202262	Age (Ma) 78.344 19.424 14.342 28.558 36.743	1s.d. 3.886 1.028 0.673 0.59 0.358
step 1 2 3 4 5 6	T (C) 525 565 605 645 700 750	t (min.) 12 12 12 12 12 12 12 12 12	36Ar 6.045 3.312 6.025 5.63 5.458 5.445	37Ar 0.978 0.846 1.69 2.035 2.593 1.975	38Ar 1.182 0.75 1.421 1.391 1.719 2.221	39Ar 3.096 7.089 19.415 21.828 50.476 90.199	40Ar 1837.198 1006.842 1842.657 1849.57 2231.325 2677.329	%40Ar* 4.7 4.9 5.3 11.9 29.4 41.3	% 39Ar rlsd 0.17488601 0.40044151 1.09670925 1.23301414 2.85127459 5.09513663	Ca/K 1.15032862 0.43448612 0.31690163 0.33941308 0.18701471 0.0797094	40Ar*/39ArK 27.8698837 6.797421 5.011902 10.0192482 12.9202262 12.2264811	Age (Ma) 78.344 19.424 14.342 28.558 36.743 34.789	1s.d. 3.886 1.028 0.673 0.59 0.358 0.389
step 1 2 3 4 5 6 7	T (C) 525 565 605 645 700 750 800	t (min.) 12 12 12 12 12 12 12 12 12 12	36Ar 6.045 3.312 6.025 5.63 5.458 5.445 6.277	37Ar 0.978 0.846 1.69 2.035 2.593 1.975 2.001	38Ar 1.182 0.75 1.421 1.391 1.719 2.221 2.434	39Ar 3.096 7.089 19.415 21.828 50.476 90.199 93.763	40Ar 1837.198 1006.842 1842.657 1849.57 2231.325 2677.329 2969.594	%40Ar* 4.7 4.9 5.3 11.9 29.4 41.3 38.9	% 39Ar rlsd 0.17488601 0.40044151 1.09670925 1.23301414 2.85127459 5.09513663 5.2964589	Ca/K 1.15032862 0.43448612 0.31690163 0.33941308 0.18701471 0.0797094 0.077689	40Ar*/39ArK 27.8698837 6.797421 5.011902 10.0192482 12.9202262 12.2264811 12.3073911	Age (Ma) 78.344 19.424 14.342 28.558 36.743 34.789 35.017	1s.d. 3.886 1.028 0.673 0.59 0.358 0.389 0.297
step 1 2 3 4 5 6 7 8	T (C) 525 565 605 645 700 750 800 850	t (min.) 12 12 12 12 12 12 12 12 12 12 12	36Ar 6.045 3.312 6.025 5.63 5.458 5.445 6.277 6.385	37Ar 0.978 0.846 1.69 2.035 2.593 1.975 2.001 2.144	38Ar 1.182 0.75 1.421 1.391 1.719 2.221 2.434 25.26	39Ar 3.096 7.089 19.415 21.828 50.476 90.199 93.763 99.064	40Ar 1837.198 1006.842 1842.657 1849.57 2231.325 2677.329 2969.594 3083.075	%40Ar* 4.7 4.9 5.3 11.9 29.4 41.3 38.9 40.2	% 39Ar rlsd 0.17488601 0.40044151 1.09670925 1.23301414 2.85127459 5.09513663 5.2964589 5.59590035	Ca/K 1.15032862 0.43448612 0.31690163 0.33941308 0.18701471 0.0797094 0.077689 0.07878671	40Ar*/39ArK 27.8698837 6.797421 5.011902 10.0192482 12.9202262 12.2264811 12.3073911 12.4806014	Age (Ma) 78.344 19.424 14.342 28.558 36.743 34.789 35.017 35.505	1s.d. 3.886 1.028 0.673 0.59 0.358 0.389 0.297 0.322
step 1 2 3 4 5 6 7 8 9	T (C) 525 565 605 645 700 750 800 850 900	t (min.) 12 12 12 12 12 12 12 12 12 12	36Ar 6.045 3.312 6.025 5.63 5.458 5.445 6.277 6.385 6.302	37Ar 0.978 0.846 1.69 2.035 2.593 1.975 2.001 2.144 2.622	38Ar 1.182 0.75 1.421 1.391 1.719 2.221 2.434 25.26 2.58	39Ar 3.096 7.089 19.415 21.828 50.476 90.199 93.763 99.064 106.02	40Ar 1837.198 1006.842 1842.657 1849.57 2231.325 2677.329 2969.594 3083.075 3142.168	%40Ar* 4.7 4.9 5.3 11.9 29.4 41.3 38.9 40.2 42.1	% 39Ar rlsd 0.17488601 0.40044151 1.09670925 1.23301414 2.85127459 5.09513663 5.2964589 5.59590035 5.98882899	Ca/K 1.15032862 0.43448612 0.31690163 0.33941308 0.18701471 0.0797094 0.077689 0.07878671 0.09003066	40Ar*/39ArK 27.8698837 6.797421 5.011902 10.0192482 12.9202262 12.2264811 12.3073911 12.4806014 12.4486533	Age (Ma) 78.344 19.424 14.342 28.558 36.743 34.789 35.017 35.505 35.415	1s.d. 3.886 1.028 0.673 0.59 0.358 0.389 0.297 0.322 0.318
step 1 2 3 4 5 6 7 8 9 10	T (C) 525 565 645 700 750 800 850 900 945	t (min.) 12 12 12 12 12 12 12 12 12 12	36Ar 6.045 3.312 6.025 5.63 5.458 5.445 6.277 6.385 6.302 5.881	37Ar 0.978 0.846 1.69 2.035 2.593 1.975 2.001 2.144 2.622 3.006	38Ar 1.182 0.75 1.421 1.391 1.719 2.221 2.434 25.26 2.58 2.438	39Ar 3.096 7.089 19.415 21.828 50.476 90.199 93.763 99.064 106.02 98.577	40Ar 1837.198 1006.842 1842.657 1849.57 2231.325 2677.329 2969.594 3083.075 3142.168 2945.927	%40Ar* 4.7 4.9 5.3 11.9 29.4 41.3 38.9 40.2 42.1 42.4	% 39Ar rlsd 0.17488601 0.40044151 1.09670925 1.23301414 2.85127459 5.09513663 5.2964589 5.59590035 5.98882899 5.56839082	Ca/K 1.15032862 0.43448612 0.31690163 0.33941308 0.18701471 0.0797094 0.077689 0.07878671 0.09003066 0.11100988	40Ar*/39ArK 27.8698837 6.797421 5.011902 10.0192482 12.9202262 12.2264811 12.3073911 12.4806014 12.4486533 12.6353945	Age (Ma) 78.344 19.424 14.342 28.558 36.743 34.789 35.017 35.505 35.415 35.941	1s.d. 3.886 1.028 0.673 0.59 0.358 0.389 0.297 0.318 0.284
step 1 2 3 4 5 6 7 8 9 10 11	T (C) 525 565 605 645 700 750 800 850 900 945 985	t (min.) 12 12 12 12 12 12 12 12 12 12	36Ar 6.045 3.312 6.025 5.63 5.458 5.445 6.277 6.385 6.302 5.881 5.574	37Ar 0.978 0.846 1.69 2.035 2.593 1.975 2.001 2.144 2.622 3.006 2.745	38Ar 1.182 0.75 1.421 1.391 1.719 2.221 2.434 25.26 2.58 2.438 2.689	39Ar 3.096 7.089 19.415 21.828 50.476 90.199 93.763 99.064 106.02 98.577 125.419	40Ar 1837.198 1006.842 1842.657 1849.57 2231.325 2677.329 2969.594 3083.075 3142.168 2945.927 3193.82	%40Ar* 4.7 4.9 5.3 11.9 29.4 41.3 38.9 40.2 42.1 42.4 49.7	% 39Ar rlsd 0.17488601 0.40044151 1.09670925 1.23301414 2.85127459 5.09513663 5.2964589 5.59590035 5.98882899 5.56839082 7.08463443	Ca/K 1.15032862 0.43448612 0.31690163 0.33941308 0.18701471 0.0797094 0.077689 0.07878671 0.09003066 0.11100988 0.0796752	40Ar*/39ArK 27.8698837 6.797421 5.011902 10.0192482 12.9202262 12.2264811 12.3073911 12.4806014 12.4486533 12.6353945 12.6236772	Age (Ma) 78.344 19.424 14.342 28.558 36.743 34.789 35.017 35.505 35.415 35.941 35.908	1s.d. 3.886 1.028 0.673 0.59 0.358 0.389 0.297 0.322 0.318 0.284 0.3
step 1 2 3 4 5 6 7 8 9 10 11 12	T (C) 525 565 645 700 750 800 850 900 945 985 1030	t (min.) 12 12 12 12 12 12 12 12 12 12	36Ar 6.045 3.312 6.025 5.63 5.458 5.445 6.277 6.385 6.302 5.881 5.574 5.51	37Ar 0.978 0.846 1.69 2.035 2.593 1.975 2.001 2.144 2.622 3.006 2.745 2.206	38Ar 1.182 0.75 1.421 1.391 1.719 2.221 2.434 25.26 2.58 2.438 2.689 3.738	39Ar 3.096 7.089 19.415 21.828 50.476 90.199 93.763 99.064 106.02 98.577 125.419 207.485	40Ar 1837.198 1006.842 1842.657 1849.57 2231.325 2677.329 2969.594 3083.075 3142.168 2945.927 3193.82 4199.144	%40Ar* 4.7 4.9 5.3 11.9 29.4 41.3 38.9 40.2 42.1 42.4 49.7 62.2	% 39Ar rlsd 0.17488601 0.40044151 1.09670925 1.23301414 2.85127459 5.09513663 5.2964589 5.59590035 5.98882899 5.56839082 7.08463443 11.7203564	Ca/K 1.15032862 0.43448612 0.31690163 0.33941308 0.18701471 0.0797094 0.077689 0.07878671 0.09003066 0.11100988 0.0796752 0.03870416	40Ar*/39ArK 27.8698837 6.797421 5.011902 10.0192482 12.9202262 12.2264811 12.3073911 12.4806014 12.4486533 12.6353945 12.6236772 12.5768101	Age (Ma) 78.344 19.424 14.342 28.558 36.743 34.789 35.017 35.505 35.415 35.941 35.908 35.776	1s.d. 3.886 1.028 0.673 0.59 0.358 0.389 0.297 0.318 0.284 0.3 0.244
step 1 2 3 4 5 6 7 8 9 10 11 12 13	T (C) 525 565 605 645 700 750 800 850 900 945 985 1030 1070	t (min.) 12 12 12 12 12 12 12 12 12 12	36Ar 6.045 3.312 6.025 5.63 5.458 5.445 6.277 6.385 6.302 5.881 5.574 5.51 5.601	37Ar 0.978 0.846 1.69 2.035 2.593 1.975 2.001 2.144 2.622 3.006 2.745 2.206 2.144	38Ar 1.182 0.75 1.421 1.391 1.719 2.221 2.434 25.26 2.58 2.438 2.689 3.738 4.556	39Ar 3.096 7.089 19.415 21.828 50.476 90.199 93.763 99.064 106.02 98.577 125.419 207.485 266.986	40Ar 1837.198 1006.842 1842.657 1849.57 2231.325 2677.329 2969.594 3083.075 3142.168 2945.927 3193.82 4199.144 4883.63	%40Ar* 4.7 4.9 5.3 11.9 29.4 41.3 38.9 40.2 42.1 42.4 49.7 62.2 66.9	% 39Ar rlsd 0.17488601 0.40044151 1.09670925 1.23301414 2.85127459 5.09513663 5.2964589 5.59590035 5.98882899 5.56839082 7.08463443 11.7203564 15.0814327	Ca/K 1.15032862 0.43448612 0.31690163 0.33941308 0.18701471 0.0797094 0.077689 0.07878671 0.09003066 0.11100988 0.0796752 0.03870416 0.02923303	40Ar*/39ArK 27.8698837 6.797421 5.011902 10.0192482 12.9202262 12.2264811 12.3073911 12.4806014 12.4486533 12.6353945 12.6236772 12.5768101 12.2442236	Age (Ma) 78.344 19.424 14.342 28.558 36.743 34.789 35.017 35.505 35.415 35.941 35.908 35.776 34.839	1s.d. 3.886 1.028 0.673 0.59 0.358 0.389 0.297 0.322 0.318 0.284 0.3 0.244 0.236
step 1 2 3 4 5 6 7 8 9 10 11 12 13 14	T (C) 525 565 605 645 700 750 800 850 900 945 985 1030 1070 1115	t (min.) 12 12 12 12 12 12 12 12 12 12	36Ar 6.045 3.312 6.025 5.63 5.458 5.445 6.277 6.385 6.302 5.881 5.574 5.51 5.601 5.73	37Ar 0.978 0.846 1.69 2.035 2.593 1.975 2.001 2.144 2.622 3.006 2.745 2.206 2.144 3.035	38Ar 1.182 0.75 1.421 1.391 1.719 2.221 2.434 25.26 2.58 2.438 2.689 3.738 4.556 4.806	39Ar 3.096 7.089 19.415 21.828 50.476 90.199 93.763 99.064 106.02 98.577 125.419 207.485 266.986 281.645	40Ar 1837.198 1006.842 1842.657 1849.57 2231.325 2677.329 2969.594 3083.075 3142.168 2945.927 3193.82 4199.144 4883.63 5076.743	%40Ar* 4.7 4.9 5.3 11.9 29.4 41.3 38.9 40.2 42.1 42.4 49.7 62.2 66.9 67.4	% 39Ar risd 0.17488601 0.40044151 1.09670925 1.23301414 2.85127459 5.09513663 5.2964589 5.59590035 5.98882899 5.56839082 7.08463443 11.7203564 15.0814327 15.9094863	Ca/K 1.15032862 0.43448612 0.31690163 0.33941308 0.18701471 0.0797094 0.077689 0.07878671 0.09003066 0.11100988 0.0796752 0.03870416 0.02923303 0.03922794	40Ar*/39ArK 27.8698837 6.797421 5.011902 10.0192482 12.9202262 12.2264811 12.3073911 12.4806014 12.4486533 12.6353945 12.6236772 12.5768101 12.2442236 12.155161	Age (Ma) 78.344 19.424 14.342 28.558 36.743 34.789 35.017 35.505 35.415 35.941 35.908 35.776 34.839 34.588	1s.d. 3.886 1.028 0.673 0.59 0.358 0.389 0.297 0.322 0.318 0.284 0.3 0.244 0.236 0.233
step 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15	T (C) 525 565 605 645 700 750 800 850 900 945 985 1030 1115 1155	t (min.) 12 12 12 12 12 12 12 12 12 12	36Ar 6.045 3.312 6.025 5.63 5.458 5.445 6.277 6.385 6.302 5.881 5.574 5.51 5.601 5.73 5.419	37Ar 0.978 0.846 1.69 2.035 2.593 1.975 2.001 2.144 2.622 3.006 2.745 2.206 2.144 3.035 3.889	38Ar 1.182 0.75 1.421 1.391 1.719 2.221 2.434 25.26 2.58 2.438 2.689 3.738 4.556 4.806 3.622	39Ar 3.096 7.089 19.415 21.828 50.476 90.199 93.763 99.064 106.02 98.577 125.419 207.485 266.986 281.645 198.711	40Ar 1837.198 1006.842 1842.657 1849.57 2231.325 2677.329 2969.594 3083.075 3142.168 2945.927 3193.82 4199.144 4883.63 5076.743 3961.701	%40Ar* 4.7 4.9 5.3 11.9 29.4 41.3 38.9 40.2 42.1 42.4 49.7 62.2 66.9 67.4 60.5	% 39Ar rlsd 0.17488601 0.40044151 1.09670925 1.23301414 2.85127459 5.09513663 5.2964589 5.59590035 5.98882899 5.56839082 7.08463443 11.7203564 15.0814327 15.9094863 11.224733	Ca/K 1.15032862 0.43448612 0.31690163 0.33941308 0.18701471 0.0797094 0.077689 0.07878671 0.09003066 0.11100988 0.0796752 0.03870416 0.02923303 0.03922794 0.07124577	40Ar*/39ArK 27.8698837 6.797421 5.011902 10.0192482 12.9202262 12.2264811 12.3073911 12.4806014 12.4486533 12.6353945 12.6236772 12.5768101 12.2442236 12.155161 12.0593703	Age (Ma) 78.344 19.424 14.342 28.558 36.743 34.789 35.017 35.505 35.415 35.941 35.908 35.776 34.839 34.588 34.318	1s.d. 3.886 1.028 0.673 0.59 0.358 0.389 0.297 0.322 0.318 0.284 0.3 0.244 0.233 0.252
step 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16	T (C) 525 565 605 645 700 750 800 850 900 945 985 1030 1115 1155 1400	t (min.) 12 12 12 12 12 12 12 12 12 12	36Ar 6.045 3.312 6.025 5.63 5.458 5.445 6.277 6.385 6.302 5.881 5.574 5.51 5.601 5.73 5.419 5.416	37Ar 0.978 0.846 1.69 2.035 2.593 1.975 2.001 2.144 2.622 3.006 2.745 2.206 2.144 3.035 3.889 8.569	38Ar 1.182 0.75 1.421 1.391 1.719 2.221 2.434 25.26 2.58 2.438 2.689 3.738 4.556 4.806 3.622 2.42	39Ar 3.096 7.089 19.415 21.828 50.476 90.199 93.763 99.064 106.02 98.577 125.419 207.485 266.986 281.645 198.711 100.523	40Ar 1837.198 1006.842 1842.657 1849.57 2231.325 2677.329 2969.594 3083.075 3142.168 2945.927 3193.82 4199.144 4883.63 5076.743 3961.701 2802.687	%40Ar* 4.7 4.9 5.3 11.9 29.4 41.3 38.9 40.2 42.1 42.4 49.7 62.2 66.9 67.4 60.5 44.3	% 39Ar rlsd 0.17488601 0.40044151 1.09670925 1.23301414 2.85127459 5.09513663 5.2964589 5.59590035 5.98882899 5.56839082 7.08463443 11.7203564 15.0814327 15.9094863 11.224733 5.67831594	Ca/K 1.15032862 0.43448612 0.31690163 0.33941308 0.18701471 0.0797094 0.077689 0.07878671 0.09003066 0.11100988 0.0796752 0.03870416 0.02923303 0.03922794 0.07124577 0.31034089	40Ar*/39ArK 27.8698837 6.797421 5.011902 10.0192482 12.9202262 12.2264811 12.3073911 12.4806014 12.4486533 12.6353945 12.6236772 12.5768101 12.2442236 12.155161 12.0593703 12.3155537	Age (Ma) 78.344 19.424 14.342 28.558 36.743 34.789 35.017 35.505 35.415 35.941 35.908 35.776 34.839 34.588 34.318 35.04	1s.d. 3.886 1.028 0.673 0.59 0.358 0.389 0.297 0.322 0.318 0.284 0.3 0.244 0.233 0.252 0.272
step 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16	T (C) 525 565 605 645 700 750 800 850 900 945 985 1030 1070 1115 1155 1400	t (min.) 12 12 12 12 12 12 12 12 12 12	36Ar 6.045 3.312 6.025 5.63 5.458 5.445 6.277 6.385 6.302 5.881 5.574 5.51 5.601 5.73 5.419 5.416	37Ar 0.978 0.846 1.69 2.035 2.593 1.975 2.001 2.144 2.622 3.006 2.745 2.206 2.144 3.035 3.889 8.569	38Ar 1.182 0.75 1.421 1.391 1.719 2.221 2.434 25.26 2.58 2.438 2.689 3.738 4.556 4.806 3.622 2.42	39Ar 3.096 7.089 19.415 21.828 50.476 90.199 93.763 99.064 106.02 98.577 125.419 207.485 266.986 281.645 198.711 100.523 Cumulative	40Ar 1837.198 1006.842 1842.657 1849.57 2231.325 2677.329 2969.594 3083.075 3142.168 2945.927 3193.82 4199.144 4883.63 5076.743 3961.701 2802.687 • %39Ar risc	%40Ar* 4.7 4.9 5.3 11.9 29.4 41.3 38.9 40.2 42.1 42.4 49.7 62.2 66.9 67.4 60.5 44.3	% 39Ar rlsd 0.17488601 0.40044151 1.09670925 1.23301414 2.85127459 5.09513663 5.2964589 5.59590035 5.9882899 5.56839082 7.08463443 11.7203564 15.0814327 15.9094863 11.224733 5.67831594	Ca/K 1.15032862 0.43448612 0.31690163 0.33941308 0.18701471 0.0797094 0.077689 0.07878671 0.09003066 0.11100988 0.0796752 0.03870416 0.02923303 0.03922794 0.07124577 0.31034089	40Ar*/39ArK 27.8698837 6.797421 5.011902 10.0192482 12.9202262 12.2264811 12.3073911 12.4806014 12.4486533 12.6353945 12.6236772 12.5768101 12.2442236 12.155161 12.0593703 12.3155537 Total gas age	Age (Ma) 78.344 19.424 14.342 28.558 36.743 34.789 35.017 35.505 35.415 35.941 35.908 35.776 34.839 34.588 34.318 35.04 34.84397	1s.d. 3.886 1.028 0.673 0.59 0.358 0.397 0.322 0.318 0.284 0.3 0.244 0.233 0.252 0.272 0.21177

APPENDIX C. Continued

Esc9Bt, biotite (D17Btcoarsegrained), 9.87 mg, J = 0.0015955+/- 0.5%

2000	DI, 010		Bicourse	, grunicu,	, 0 .07 m	9,0 0.00	10000.7 0.0	,,0					
step	T (C)	t (min.)	36Ar	37Ar	38Ar	39Ar	40Ar	%40Ar*	% 39Ar rlsd	Ca/K	40Ar*/39ArK	Age (Ma)	1s.d.
1	525	12	6.877	0.588	1.38	5.871	2054.687	3.1	0.39149396	0.37775985	10.9908724	31.362	1.335
2	565	12	3.565	0.772	0.848	11.908	1082.27	4.7	0.79405724	0.24451844	4.24862448	12.188	0.536
3	605	12	8.651	2.017	2.28	40.417	2608.579	3.9	2.69511349	0.1882208	2.55382237	7.336	0.225
4	645	12	6.474	1.808	1.702	33.197	1979.857	5.3	2.21366461	0.20541286	3.17295148	9.11	0.337
5	700	12	2.599	2.438	0.848	25.224	1009.852	25.7	1.68200368	0.36455962	10.2662419	29.311	0.294
6	750	12	2.916	1.476	1.213	46.995	1455.669	42.2	3.1337521	0.11845445	13.0629533	37.214	0.227
7	800	12	3.289	1.047	1.571	69.162	1839.585	48.4	4.61190686	0.05709365	12.8743045	36.682	0.224
8	850	12	1.884	1.413	1.51	80.623	1601.881	66.2	5.37615694	0.06609872	13.1512686	37.463	0.216
9	900	12	1.445	2.199	1.578	97.899	1725.446	76	6.52816676	0.08471479	13.4003195	38.165	0.219
10	945	12	1.009	2.407	1.379	87.406	1473.627	80.5	5.8284655	0.10386031	13.5699567	38.643	0.218
11	985	12	0.892	1.897	1.621	107.286	1728.36	85.4	7.15411699	0.06668593	13.752775	39.158	0.219
12	1030	12	0.938	1.668	2.438	171.214	2632.304	89.8	11.4170067	0.036742	13.8337288	39.386	0.22
13	1070	12	0.751	1.013	3.223	229.098	3304.946	93.5	15.2768664	0.01667599	13.5188479	38.499	0.215
14	1115	12	0.699	0.549	39.5	284.453	3892.515	94.9	18.9680857	0.00727887	13.0115304	37.069	0.209
15	1155	12	0.416	0.225	2.098	148.366	1992.141	94.2	9.89344109	0.00571939	12.6559385	36.066	0.204
16	1400	12	0.421	0.282	0.88	60.516	879.994	86.8	4.03536849	0.01757448	12.5595408	35.794	0.206
						Cumulative	e %39Ar rlso	1 =	99.9996666		Total gas age	35.95114	0.19333

Esc1Bt, biotite, 9.82 mg, J = 0.001611 ± 0.5%

2001	Dt, 510	, 0.0 <u>2</u>	ing, o	0.001011	- 0.0 /0								
step	T (C)	t (min.)	36Ar	37Ar	38Ar	39Ar	40Ar	%40Ar*	% 39Ar rlsd	Ca/K	40Ar*/39ArK	Age (Ma)	1s.d.
1	560	12	9.405	0.294	1.79	2.064	2941.855	7.4	0.11104117	0.59716223	106.736085	286.254	4.788
2	620	12	5.962	0.481	1.217	5.692	1865.306	7.5	0.30622401	0.35424453	24.5870201	70.08	2.553
3	680	12	2.991	0.295	0.654	6.857	971.684	11	0.36889986	0.18033836	15.5661431	44.683	0.557
4	740	12	2.959	0.352	0.766	17.703	1085.182	21.2	0.95240401	0.08334573	12.9822308	37.342	0.306
5	800	12	2.565	0.458	1.359	63.512	1515.775	51.2	3.41688321	0.03022667	12.2197356	35.17	0.225
6	850	12	1.236	0.568	1.77	114.989	1761.252	79.9	6.18629524	0.02070482	12.2481548	35.251	0.205
7	900	12	0.914	1.012	2.537	175.977	2438.287	89.3	9.46738973	0.02410485	12.3941298	35.667	0.202
8	945	12	0.75	1.206	2.258	157.855	2176.767	90.2	8.49244393	0.03202358	12.4576535	35.848	0.204
9	995	12	0.703	1.973	2.362	164.676	2248.563	91.2	8.85940703	0.05022038	12.4625672	35.862	0.205
10	1040	12	0.894	1.387	2.483	169.298	2372.569	89.3	9.10806609	0.03434044	12.5285549	36.05	0.205
11	1085	12	0.885	1.675	2.632	185.271	2551.862	90.1	9.9673978	0.03789562	12.4330856	35.778	0.203
12	1130	12	0.898	2.593	2.564	175.819	2453.766	88.5	9.45888948	0.06181893	12.3685116	35.594	0.202
13	1180	12	0.748	4.473	2.965	209.89	2788.405	92.4	11.2918758	0.08932962	12.294821	35.384	0.202
14	1225	12	0.535	9.317	3.115	223.368	2895.901	94.8	12.016979	0.17484558	12.3162255	35.445	0.201
15	1265	12	0.338	11.347	1.995	142.178	1847.952	95.1	7.64903673	0.33455617	12.3625458	35.577	0.202
16	1400	12	0.341	3.599	0.638	43.625	642.473	85.7	2.34698214	0.34583446	12.5124084	36.004	0.218
						Cumulative	e %39Ar riso	1 =	100.000215	no plateau	Total gas age	36.07129	0.18771

APPENDIX C. Ar-Ar ISOTOPIC DATA AND AGES APPENDIX C. Continued

Esc2Bt, biotite, 11.10 mg, J = 0.001612 ± 0.5%

step	T (C)	t (min.)	36Ar	37Ar	38Ar	39Ar	40Ar	%40Ar*	% 39Ar rlsd	Ca/K	40Ar*/39ArK	Age (Ma)	1s.d.
1	560	12	8.687	1.722	1.716	3.341	2649.227	5.4	0.25809591	2.11772639	42.9864702	120.871	3.682
2	620	12	4.813	3.728	1.056	8.871	1501.255	7.8	0.68529448	1.72649537	13.2670208	38.176	0.906
3	680	12	5.05	2.454	1.138	12.595	1634.633	11.1	0.97297757	0.80023494	14.4851414	41.641	0.526
4	740	12	9.551	3.334	2.173	28.66	3178.387	13.3	2.21401644	0.47773648	14.7642497	42.434	0.632
5	800	12	8.865	6.112	2.742	77.023	3491.033	26.7	5.95011124	0.32586827	12.1557066	35.009	0.243
6	850	12	1.68	4.566	1.642	102.559	1737.044	72.8	7.92279525	0.18281954	12.3296264	35.505	0.206
7	900	12	0.884	3.15	1.996	139.309	2000.682	87.9	10.7617731	0.09284961	12.634101	36.373	0.206
8	945	12	1.166	3.531	1.961	129.484	1943.573	83.3	10.002781	0.11197803	12.5179765	36.042	0.205
9	990	12	1.34	5.924	1.854	119.303	1883.291	80.1	9.21628762	0.20390455	12.6590127	36.444	0.208
10	1035	12	1.536	8.713	1.655	104.603	1781.451	75.8	8.0806965	0.34206202	12.922224	37.194	0.215
11	1085	12	1.877	18.221	2.151	137.542	2259.884	76.6	10.6252704	0.54405717	12.6067344	36.295	0.209
12	1135	12	1.439	18.684	2.132	140.822	2151.808	80.9	10.878654	0.54488785	12.3822325	35.655	0.205
13	1175	12	1.043	28.101	1.662	110.796	1658.242	82.3	8.55911254	1.04176645	12.3226125	35.485	0.203
14	1400	12	0.939	45.926	2.597	179.567	2472.545	89.4	13.8717477	1.05052384	12.3313798	35.51	0.202
						Cumulative	e %39Ar risc	1 =	99.9996137	no plateau	Total gas age	36.39648	0.19179

Esc5	Bt, bio	tite, 12.6	5 mg, J =	0.001610)5 ± 0.59	%							
step	T (C)	t (min.)	36Ar	37Ar	38Ar	39Ar	40Ar	%40Ar*	% 39Ar rlsd	Ca/K	40Ar*/39ArK	Age (Ma)	1s.d.
1	560	12	27.518	0.427	5.422	19.743	8344.884	4.5	2.619512	0.08624879	19.0056402	54.392	1.424
2	620	12	17.404	0.519	3.67	28.443	5424.418	7.1	3.77383274	0.072766	13.5237446	38.871	0.686
3	680	12	17.995	0.527	3.877	40.149	5826.691	10.5	5.3269912	0.05234434	15.3550928	44.071	0.521
4	740	12	24.995	0.993	5.76	99.061	8637.598	16.2	13.1434675	0.03997411	14.149331	40.649	0.387
5	785	12	9.271	0.875	3.041	103.634	3989.022	32.7	13.7502156	0.03366954	12.6198809	36.299	0.246
6	830	12	10.996	1.051	3.647	120.787	4558.821	30.1	16.026085	0.03469877	11.4073852	32.843	0.233
7	880	12	6.43	1.141	2.932	134.916	3493.567	46.7	17.9007284	0.03372513	12.1277261	34.897	0.212
8	925	12	3.307	1.001	2.076	114.103	2328.904	59	15.1392482	0.03498393	12.0557955	34.692	0.215
9	970	12	1.927	1.074	1.22	61.855	1258.5	56	8.20695511	0.06924135	11.3691816	32.734	0.196
10	1020	12	2.635	2.265	0.876	20.914	948.943	19.8	2.77488092	0.43193116	8.95932366	25.845	0.327
11	1065	12	2.24	5.074	0.544	6.356	701.646	7.8	0.84331754	3.18646892	8.60434328	24.828	0.625
12	1110	12	0.944	6.427	0.22	1.656	295.052	8.1	0.21971898	15.5489715	14.2267806	40.869	1.205
13	1155	12	0.498	13.629	0.104	0.742	154.771	9	0.09844896	74.8968491	18.5184492	53.018	3.927
14	1400	12	0.698	50.634	0.201	1.334	222.924	13	0.17699585	158.581538	22.1547072	63.248	2.423
						Cumulativ	e %39Ar rlsd	=	100.000398	no plateau	Total gas age	36.20259	0.20417

APPENDIX C. Ar-Ar ISOTOPIC DATA AND AGES. Continued

Esc28ALU, alunite, 9.92 mg, J = 0.001610 ± 0.5%

4 amu discrimination = $1.01684 \pm 0.42\%$, $40/39K = 0.02207 \pm 129.0\%$, $36/37Ca = 0.0002786 \pm 0.32\%$, $39/37Ca = 0.0006784 \pm 0.43\%$

step	T (C)	t (min.)	36Ar	37Ar	38Ar	39Ar	40Ar	%40Ar*	% 39Ar rlsd	Ca/K	40Ar*/39ArK	Age (Ma)	1s.d.
1	450	12	6.757	0.11	1.572	17.788	2285.901	14.4	0.84505972	0.02654453	18.59227821	53.21	0.495
2	470	12	1.841	0.156	0.865	39.474	831.668	36.2	1.87530286	0.01696374	7.599049468	21.938	0.159
3	490	12	1.539	0.222	1.087	62.065	947.438	53.3	2.9485401	0.01535374	8.115386716	23.419	0.179
4	505	12	1.215	0.256	1.293	82.522	1186.041	70.7	3.92039678	0.01331613	10.14228947	29.221	0.183
5	515	12	0.765	0.314	1.685	120.846	1567.941	86.2	5.74106625	0.01115334	11.18026799	32.185	0.187
6	525	12	0.475	0.409	2.516	187.702	2349.057	94.3	8.91721379	0.00935323	11.82092466	34.012	0.195
7	540	12	0.583	0.676	4.83	363.091	4583.327	96.3	17.2494703	0.00799168	12.19573063	35.08	0.201
8	550	12	0.517	0.876	6.478	494.071	6217.527	97.6	23.4719754	0.00761065	12.3189597	35.431	0.204
9	560	12	0.637	0.906	6.718	507.966	6435.546	97.1	24.1320893	0.00765598	12.34353816	35.501	0.202
10	570	12	0.337	0.462	2.905	220.154	2786.46	96.6	10.4589204	0.00900788	12.25365584	35.245	0.202
11	590	12	0.165	0.102	0.173	8.813	134.446	69	0.41868177	0.04968084	9.984151052	28.769	0.224
12	1000	12	3.985	0.454	0.769	0.448	1176.454	2	0.02128327	4.35564548	52.93714607	147.557	10.122
						Cumulative	e %39Ar rlsd =	=	100		Total gas age =	34.3505477	0.21049811
										Steps 8 - 10	Plateau age =	35.3934882	0.21049811

Esc2	Esc29ALU, alunite, 10.65 mg, J = 0.0016106 ± 0.5%												
step	T (C)	t (min.)	36Ar	37Ar	38Ar	39Ar	40Ar	%40Ar*	% 39Ar rlsd	Ca/K	40Ar*/39ArK	Age (Ma)	1s.d.
1	450	12	8.609	0.112	1.791	6.648	2810.672	11.3	0.3083631	0.07391205	48.18859116	134.48	1.607
2	470	12	5.811	0.123	1.362	16.991	1978.671	15	0.78811633	0.03175915	17.55814275	50.168	0.555
3	490	12	4.765	0.197	1.427	39.24	1827.904	24.6	1.82012153	0.02202514	11.49945519	33.014	0.377
4	505	12	3.568	0.22	1.362	49.738	1603.201	35.7	2.30706434	0.01940508	11.54128713	33.133	0.254
5	515	12	2.723	0.24	1.294	57.648	1461.112	46.2	2.67396447	0.01826451	11.7501366	33.727	0.214
6	525	12	2.254	0.272	1.411	77.69	1571.199	58.7	3.60359942	0.01535976	11.90382902	34.164	0.205
7	535	12	2.026	0.323	1.795	106.716	1865.059	68.7	4.9499513	0.01327863	12.05896599	34.605	0.203
8	545	12	1.965	0.393	2.29	146.66	2365.397	76.1	6.8027274	0.01175604	12.32817109	35.37	0.21
9	555	12	2.238	0.593	3.826	259.972	3847.072	83.2	12.0586298	0.01000709	12.38237782	35.524	0.203
10	565	12	2.776	0.857	5.705	403.37	5777.031	86.1	18.7100515	0.00932088	12.40490665	35.588	0.204
11	575	12	3.405	1.124	7.31	512.639	7320.07	86.5	23.778422	0.0096191	12.43130865	35.663	0.204
12	585	12	3.012	0.916	5.179	352.772	5245.205	83.4	16.3630966	0.01139151	12.47285	35.781	0.204
13	595	12	1.624	0.488	1.772	108.621	1838.348	74.6	5.03831347	0.01971003	12.67989321	36.369	0.209
14	1000	12	13.945	14.392	2.907	17.196	4473.219	9.8	0.79762512	3.67580325	25.60757773	72.709	1.38
						Cumulative	e %39Ar rlsd :	=	100.000046		Total gas age =	33.7046195	0.19055671
Note:	isotope	beams i	n mV rls	d = relea	sed, err	or in age in	cludes 0.5% .	l error, all er	rors 1 sigma		Plateau age =	35.2106061	0.19055671
(Not o	correcte	d for dec	ay)								Steps 9 - 12		

APPENDIX C. Ar-Ar ISOTOPIC DATA AND AGES. Continued

			,	0/									
step	T (C)	t (min.)	36Ar	37Ar	38Ar	39Ar	40Ar	%40Ar*	% 39Ar rlsd	Ca/K	40Ar*/39ArK	Age (Ma)	1s.d.
1	450	12	60.833	0.355	16.969	21.598	18325.1	3.7	1.516681531	0.135299489	31.70913784	117.481	6.09
2	485	12	23.679	0.324	8.493	25.174	7277.364	5.6	1.767799836	0.105942517	16.29173347	61.315	2.184
3	530	12	12.437	0.519	6.677	56.343	4118.98	12.4	3.956587993	0.075822999	9.073373536	34.405	0.565
4	575	12	3.713	0.455	3.622	71.056	1798.944	40.3	4.989782519	0.052708565	10.15261102	38.454	0.297
5	615	12	2.204	0.66	4.404	130.966	2150.887	70.5	9.196856808	0.0414815	11.54701559	43.672	0.264
6	650	12	1.592	0.639	3.874	139.298	2067.553	78	9.781956841	0.037759356	11.53283213	43.619	0.257
7	685	12	7.552	0.702	5.377	162.025	3999.293	45.2	11.37792041	0.035663454	11.17089359	42.266	0.287
8	715	12	6.1	0.526	4.114	133.951	3203.934	44.9	9.406473178	0.032322703	10.73441413	40.633	0.299
9	755	12	1.458	0.614	4.33	212.093	2552.607	83.7	14.89385757	0.023829164	10.05655697	38.094	0.216
10	855	12	1.403	0.599	4.38	222.107	2519.876	84.1	15.5970731	0.022198884	9.525670712	36.103	0.205
11	1000	12	2.859	0.72	4.45	206.757	2771.36	70.4	14.51914637	0.028664191	9.403631076	35.645	0.21
12	1200	12	3.328	0.931	2.513	41.242	1395.739	31.5	2.896146851	0.18582233	10.44435925	39.547	0.362
13	1400	12	1.013	0.071	0.774	1.424	305.657	4.4	0.099997893	0.410455088	7.936257161	30.129	2.784
						Cumulative	e %39Ar rlsd	=	100.0002809	no plateau	Total gas age =	40.71564	0.215
Esc1	5Ser, d	ark seric	ite, 15.84	mg, J =	0.002128	3 ± 0.5%							
step	T (C)	t (min.)	36Ar	37Ar	38Ar	39Ar	40Ar	%40Ar*	% 39Ar rlsd	Ca/K	40Ar*/39ArK	Age (Ma)	1s.d.
1	450	12	31.427	0.233	10.028	26 04	9511 74	11	4 004000050	0.066142272	14 04502045	FC 40F	0.00
-							0011.11	4.1	1.081399358	0.000143273	14.94592945	50.485	2.30
2	470	12	14.92	0.109	5.182	19.906	4593.406	5.7	1.285327789	0.066143273	13.16595647	56.485 49.85	2.36 1.515
2 3	470 510	12 12	14.92 15.009	0.109 0.194	5.182 6.154	19.906 43.92	4593.406 4756.265	4.1 5.7 8.4	1.285327789 2.835908595	0.066143273 0.040477146 0.032651697	13.16595647 9.080447654	56.485 49.85 34.528	2.36 1.515 0.883
2 3 4	470 510 540	12 12 12	14.92 15.009 10.9	0.109 0.194 0.252	5.182 6.154 5.408	19.906 43.92 72.86	4593.406 4756.265 3772.76	5.7 8.4 16.1	1.285327789 2.835908595 4.70456057	0.066143273 0.040477146 0.032651697 0.025566826	13.16595647 9.080447654 8.343156104	56.485 49.85 34.528 31.749	2.36 1.515 0.883 0.393
2 3 4 5	470 510 540 565	12 12 12 12	14.92 15.009 10.9 9.737	0.109 0.194 0.252 0.243	5.182 6.154 5.408 4.759	19.906 43.92 72.86 100.497	4593.406 4756.265 3772.76 3843.079	5.7 8.4 16.1 26.4	1.285327789 2.835908595 4.70456057 6.489078007	0.066143273 0.040477146 0.032651697 0.025566826 0.017873829	14.34332343 13.16595647 9.080447654 8.343156104 10.11467214	56.485 49.85 34.528 31.749 38.419	2.36 1.515 0.883 0.393 0.327
2 3 4 5 6	470 510 540 565 585	12 12 12 12 12	14.92 15.009 10.9 9.737 7.565	0.109 0.194 0.252 0.243 0.183	5.182 6.154 5.408 4.759 3.833	19.906 43.92 72.86 100.497 99.639	4593.406 4756.265 3772.76 3843.079 3324.462	5.7 8.4 16.1 26.4 34	1.285327789 2.835908595 4.70456057 6.489078007 6.43367706	0.006143273 0.040477146 0.032651697 0.025566826 0.017873829 0.013576431	13.16595647 9.080447654 8.343156104 10.11467214 11.32902499	56.485 49.85 34.528 31.749 38.419 42.977	2.36 1.515 0.883 0.393 0.327 0.312
2 3 4 5 6 7	470 510 540 565 585 610	12 12 12 12 12 12 12	14.92 15.009 10.9 9.737 7.565 6.875	0.109 0.194 0.252 0.243 0.183 0.217	5.182 6.154 5.408 4.759 3.833 4.116	19.906 43.92 72.86 100.497 99.639 128.097	4593.406 4756.265 3772.76 3843.079 3324.462 3480.875	5.7 8.4 16.1 26.4 34 42.7	1.285327789 2.835908595 4.70456057 6.489078007 6.43367706 8.271206359	0.000145273 0.040477146 0.032651697 0.025566826 0.017873829 0.013576431 0.012522312	13.16595647 9.080447654 8.343156104 10.11467214 11.32902499 11.60039538	56.485 49.85 34.528 31.749 38.419 42.977 43.994	2.36 1.515 0.883 0.393 0.327 0.312 0.291
2 3 4 5 6 7 8	470 510 540 565 585 610 630	12 12 12 12 12 12 12 12	14.92 15.009 10.9 9.737 7.565 6.875 5.961	0.109 0.194 0.252 0.243 0.183 0.217 0.192	5.182 6.154 5.408 4.759 3.833 4.116 3.733	19.906 43.92 72.86 100.497 99.639 128.097 127.099	4593.406 4756.265 3772.76 3843.079 3324.462 3480.875 3209.35	4.1 5.7 8.4 16.1 26.4 34 42.7 46.1	1.285327789 2.835908595 4.70456057 6.489078007 6.43367706 8.271206359 8.206765631	0.000143273 0.040477146 0.032651697 0.025566826 0.017873829 0.013576431 0.012522312 0.011166644	13.16595647 9.080447654 8.343156104 10.11467214 11.32902499 11.60039538 11.64256891	56.485 49.85 34.528 31.749 38.419 42.977 43.994 44.152	2.36 1.515 0.883 0.393 0.327 0.312 0.291 0.284
2 3 4 5 6 7 8 9	470 510 540 565 585 610 630 665	12 12 12 12 12 12 12 12 12	14.92 15.009 10.9 9.737 7.565 6.875 5.961 5.902	0.109 0.194 0.252 0.243 0.183 0.217 0.192 0.228	5.182 6.154 5.408 4.759 3.833 4.116 3.733 4.824	19.906 43.92 72.86 100.497 99.639 128.097 127.099 189.428	4593.406 4756.265 3772.76 3843.079 3324.462 3480.875 3209.35 3834.273	4.1 5.7 8.4 16.1 26.4 34 42.7 46.1 55.4	1.285327789 2.835908595 4.70456057 6.489078007 6.43367706 8.271206359 8.206765631 12.23134092	0.008143273 0.040477146 0.032651697 0.025566826 0.017873829 0.013576431 0.012522312 0.011166644 0.008897212	14.94392943 13.16595647 9.080447654 8.343156104 10.11467214 11.32902499 11.60039538 11.64256891 11.2033979	56.485 49.85 34.528 31.749 38.419 42.977 43.994 44.152 42.506	2.36 1.515 0.883 0.393 0.327 0.312 0.291 0.284 0.256
2 3 4 5 6 7 8 9 10	470 510 565 585 610 630 665 700	12 12 12 12 12 12 12 12 12 12	14.92 15.009 10.9 9.737 7.565 6.875 5.961 5.902 13.865	0.109 0.194 0.252 0.243 0.183 0.217 0.192 0.228 0.301	5.182 6.154 5.408 4.759 3.833 4.116 3.733 4.824 8.578	19.906 43.92 72.86 100.497 99.639 128.097 127.099 189.428 291.404	4593.406 4756.265 3772.76 3843.079 3324.462 3480.875 3209.35 3834.273 7129.676	4.1 5.7 8.4 16.1 26.4 34 42.7 46.1 55.4 43.5	1.285327789 2.835908595 4.70456057 6.489078007 6.43367706 8.271206359 8.206765631 12.23134092 18.81591776	0.008143273 0.040477146 0.032651697 0.025566826 0.017873829 0.013576431 0.012522312 0.011166644 0.008897212 0.00763544	14.94392943 13.16595647 9.080447654 8.343156104 10.11467214 11.32902499 11.60039538 11.64256891 11.2033979 10.66072463	56.485 49.85 34.528 31.749 38.419 42.977 43.994 44.152 42.506 40.47	2.36 1.515 0.883 0.393 0.327 0.312 0.291 0.284 0.256 0.289
2 3 4 5 6 7 8 9 10 11	470 510 540 565 585 610 630 665 700 725	12 12 12 12 12 12 12 12 12 12 12	14.92 15.009 10.9 9.737 7.565 6.875 5.961 5.902 13.865 1.931	0.109 0.194 0.252 0.243 0.183 0.217 0.192 0.228 0.301 0.175	5.182 6.154 5.408 4.759 3.833 4.116 3.733 4.824 8.578 3.191	19.906 43.92 72.86 100.497 99.639 128.097 127.099 189.428 291.404 157.672	4593.406 4756.265 3772.76 3843.079 3324.462 3480.875 3209.35 3834.273 7129.676 2121.856	4.1 5.7 8.4 16.1 26.4 34 42.7 46.1 55.4 43.5 73.8	1.285327789 2.835908595 4.70456057 6.489078007 6.43367706 8.271206359 8.206765631 12.23134092 18.81591776 10.1808602	0.008143273 0.040477146 0.032651697 0.025566826 0.017873829 0.013576431 0.012522312 0.011166644 0.008897212 0.00763544 0.008204397	14.94392943 13.16595647 9.080447654 8.343156104 10.11467214 11.32902499 11.60039538 11.64256891 11.2033979 10.66072463 9.902382556	56.483 49.85 34.528 31.749 38.419 42.977 43.994 44.152 42.506 40.47 37.621	2.36 1.515 0.883 0.393 0.327 0.312 0.291 0.284 0.256 0.289 0.222
2 3 4 5 6 7 8 9 10 11 12	470 510 540 565 585 610 630 665 700 725 755	12 12 12 12 12 12 12 12 12 12 12 12	14.92 15.009 10.9 9.737 7.565 6.875 5.961 5.902 13.865 1.931 1.449	0.109 0.194 0.252 0.243 0.183 0.217 0.192 0.228 0.301 0.175 0.123	5.182 6.154 5.408 4.759 3.833 4.116 3.733 4.824 8.578 3.191 2.267	19.906 43.92 72.86 100.497 99.639 128.097 127.099 189.428 291.404 157.672 109.85	4593.406 4756.265 3772.76 3843.079 3324.462 3480.875 3209.35 3834.273 7129.676 2121.856 1479.117	4.1 5.7 8.4 16.1 26.4 34 42.7 46.1 55.4 43.5 73.8 72	1.285327789 2.835908595 4.70456057 6.489078007 6.43367706 8.271206359 8.206765631 12.23134092 18.81591776 10.1808602 7.092999981	0.008143273 0.040477146 0.032651697 0.025566826 0.017873829 0.013576431 0.012522312 0.011166644 0.008897212 0.00763544 0.008204397 0.00827691	14.94392943 13.16595647 9.080447654 8.343156104 10.11467214 11.32902499 11.60039538 11.64256891 11.2033979 10.66072463 9.902382556 9.632500745	30.483 49.85 34.528 31.749 38.419 42.977 43.994 44.152 42.506 40.47 37.621 36.606	2.36 1.515 0.883 0.393 0.327 0.312 0.291 0.284 0.256 0.289 0.222 0.209
2 3 4 5 6 7 8 9 10 11 12 13	470 540 565 585 610 630 665 700 725 755 800	12 12 12 12 12 12 12 12 12 12 12 12	14.92 15.009 10.9 9.737 7.565 6.875 5.961 5.902 13.865 1.931 1.449 1.397	0.109 0.194 0.252 0.243 0.183 0.217 0.192 0.228 0.301 0.175 0.123 0.102	5.182 6.154 5.408 4.759 3.833 4.116 3.733 4.824 8.578 3.191 2.267 1.834	19.906 43.92 72.86 100.497 99.639 128.097 127.099 189.428 291.404 157.672 109.85 87.744	4593.406 4756.265 3772.76 3843.079 3324.462 3480.875 3209.35 3834.273 7129.676 2121.856 1479.117 1225.86	4.1 5.7 8.4 16.1 26.4 34 42.7 46.1 55.4 43.5 73.8 72 67.5	1.285327789 2.835908595 4.70456057 6.489078007 6.43367706 8.271206359 8.206765631 12.23134092 18.81591776 10.1808602 7.092999981 5.665618482	0.008143273 0.040477146 0.032651697 0.025566826 0.017873829 0.013576431 0.012522312 0.011166644 0.008897212 0.00763544 0.008204397 0.00827691 0.008593023	14.94392943 13.16595647 9.080447654 8.343156104 10.11467214 11.32902499 11.60039538 11.64256891 11.2033979 10.66072463 9.902382556 9.632500745 9.342845963	30.483 49.85 34.528 31.749 38.419 42.977 43.994 44.152 42.506 40.47 37.621 36.606 35.516	2.36 1.515 0.883 0.393 0.327 0.312 0.291 0.284 0.256 0.289 0.222 0.209 0.206
2 3 4 5 6 7 8 9 10 11 12 13 14	470 540 565 585 610 630 665 700 725 755 800 860	12 12 12 12 12 12 12 12 12 12 12 12 12	14.92 15.009 10.9 9.737 7.565 6.875 5.961 5.902 13.865 1.931 1.449 1.397 1.526	0.109 0.194 0.252 0.243 0.183 0.217 0.192 0.228 0.301 0.175 0.123 0.102 0.101	5.182 6.154 5.408 4.759 3.833 4.116 3.733 4.824 8.578 3.191 2.267 1.834 1.278	19.906 43.92 72.86 100.497 99.639 128.097 127.099 189.428 291.404 157.672 109.85 87.744 54.349	4593.406 4756.265 3772.76 3843.079 3324.462 3480.875 3209.35 3834.273 7129.676 2121.856 1479.117 1225.86 945.122	4.1 5.7 8.4 16.1 26.4 34 42.7 46.1 55.4 43.5 73.8 72 67.5 53.7	1.285327789 2.835908595 4.70456057 6.489078007 6.43367706 8.271206359 8.206765631 12.23134092 18.81591776 10.1808602 7.092999981 5.665618482 3.509307746	0.008143273 0.040477146 0.032651697 0.025566826 0.017873829 0.013576431 0.012522312 0.011166644 0.008897212 0.00763544 0.008204397 0.00827691 0.008593023 0.013737057	14.94392943 13.16595647 9.080447654 8.343156104 10.11467214 11.32902499 11.60039538 11.64256891 11.2033979 10.66072463 9.902382556 9.632500745 9.342845963 9.226767449	56.485 49.85 34.528 31.749 38.419 42.977 43.994 44.152 42.506 40.47 37.621 36.606 35.516 35.079	2.36 1.515 0.883 0.393 0.327 0.312 0.291 0.284 0.256 0.289 0.222 0.209 0.206 0.285
2 3 4 5 6 7 8 9 10 11 12 13 14 15	470 540 565 585 610 630 665 700 725 755 800 860 1000	12 12 12 12 12 12 12 12 12 12 12 12 12 1	14.92 15.009 10.9 9.737 7.565 6.875 5.961 5.902 13.865 1.931 1.449 1.397 1.526 2.586	0.109 0.194 0.252 0.243 0.183 0.217 0.192 0.228 0.301 0.175 0.123 0.102 0.101 0.102	5.182 6.154 5.408 4.759 3.833 4.116 3.733 4.824 8.578 3.191 2.267 1.834 1.278 1.198	19.906 43.92 72.86 100.497 99.639 128.097 127.099 189.428 291.404 157.672 109.85 87.744 54.349 34.361	4593.406 4756.265 3772.76 3843.079 3324.462 3480.875 3209.35 3834.273 7129.676 2121.856 1479.117 1225.86 945.122 1069.162	4.1 5.7 8.4 16.1 26.4 34 42.7 46.1 55.4 43.5 73.8 72 67.5 53.7 30	1.285327789 2.835908595 4.70456057 6.489078007 6.43367706 8.271206359 8.206765631 12.23134092 18.81591776 10.1808602 7.092999981 5.665618482 3.509307746 2.218685228	0.008143273 0.040477146 0.032651697 0.025566826 0.017873829 0.013576431 0.012522312 0.011166644 0.008897212 0.00763544 0.008204397 0.00827691 0.008593023 0.013737057 0.021943169	14.94392943 13.16595647 9.080447654 8.343156104 10.11467214 11.32902499 11.60039538 11.64256891 11.2033979 10.66072463 9.902382556 9.632500745 9.342845963 9.226767449 9.248015418	56.485 49.85 34.528 31.749 38.419 42.977 43.994 44.152 42.506 40.47 37.621 36.606 35.516 35.079 35.159	2.36 1.515 0.883 0.393 0.327 0.312 0.291 0.284 0.256 0.289 0.222 0.209 0.206 0.285 0.309

Cumulative %39Ar rlsd =

Esc14Ser, dark sericite, 17.01 mg, J = 0.002122 ± 0.5%

Total gas age = 39.98499 0.213

99.99974172 no plateau

APPENDIX C. Continued

step	T (C)	t (min.)	36Ar	37Ar	38Ar	39Ar	40Ar	%40Ar*	% 39Ar rlsd	Ca/K	40Ar*/39ArK	Age (Ma)	1s.d.
1	450	12	6.577	0.215	4.14	35.928	2221.763	14.1	0.972941355	0.046531118	8.71555672	33.076	1.037
2	485	12	6.713	0.264	5.198	76.708	2606.548	25.3	2.077276371	0.026760779	8.585005888	32.585	0.311
3	530	12	5.187	0.968	7.289	259.807	3269.335	53.9	7.035653935	0.028970786	6.78353204	25.796	0.172
4	575	12	2.18	0.391	3.994	207.321	2419.701	74	5.614316818	0.014664504	8.607337931	32.669	0.19
5	615	12	4.74	0.504	7.967	449.74	5685.532	75.7	12.17909833	0.008713691	9.588313846	36.355	0.21
6	650	12	2.327	0.455	6.473	458.309	5050.05	86.6	12.4111495	0.007719444	9.549153525	36.208	0.205
7	685	12	7.58	0.346	6.802	391.87	5928.702	62.8	10.61196083	0.006865418	9.521982933	36.106	0.219
8	715	12	3.119	0.242	4.612	304.837	3794.963	76.2	8.255080266	0.006172776	9.482828016	35.959	0.209
9	755	12	1.459	0.335	8.12	606.434	6102.339	93	16.42242033	0.004295303	9.372305842	35.544	0.198
10	855	12	1.141	0.315	7.793	572.057	5600.977	94	15.49148053	0.004281577	9.219214719	34.969	0.195
11	1000	12	1.103	0.822	4.55	289.716	2980.498	89.6	7.845598908	0.022061458	9.191264217	34.864	0.196
12	1400	12	2.323	1.827	10.088	39.99	1058.457	40.8	1.082941572	0.355275734	10.29027717	38.988	0.298
						Cumulative	e %39Ar rIsd	=	99.99991876		Total gas age =	34.7812	0.1843
Note:	isotope	e beams ir	n mV rlsd	= releas	ed, error	in age inclu	des 0.5% J e	error, all er	rors 1 sigma		no plateau		
Esc2	0Ser, v	vhite seri	cite, 19.8	3 mg, J	= 0.0021	16 ± 0.5%							
step	T (C)	t (min.)	36Ar	37Ar	38Ar	39Ar	40Ar	%40Ar*	% 39Ar rlsd	Ca/K	40Ar*/39ArK	Age (Ma)	1s.d.
1	450	12	2.435	0.104	5.945	22.838	949.38	25.8	0.644756939	0.034993863	10.60010712	40.018	0.412
2	485	12	3.271	0.146	7.54	42.082	1300.265	27.2	1.188048931	0.026660728	8.323556996	31.498	0.32
3	530	12	4.936	0.278	4.291	99.416	2217.423	35.5	2.806688669	0.021488364	7.89084167	29.874	0.225
4	575	12	9.205	0.516	5.395	185.516	4214.704	36.6	5.237443219	0.02137387	8.323290426	31.497	0.232
5	615	12	9.656	1.166	6.01	282.759	5372.016	47.8	7.982784273	0.031688253	9.095363451	34.391	0.226
6	650	12	6.338	0.736	6.294	351.919	5187.289	64.5	9.935292806	0.016071235	9.519275831	35.978	0.215
7	685	12	4.018	0.494	6.254	392.572	5020.835	76.7	11.08299855	0.009669877	9.825087398	37.122	0.214
8	715	12	10.225	0.372	7.768	392.975	6899.245	57	11.09437595	0.007274297	10.02247086	37.86	0.235
9	755	12	4.662	0.476	9.782	638.597	7642.527	82.2	18.02871735	0.005727866	9.860118406	37.253	0.212
10	855	12	2.593	0.35	9.703	645.768	6960.164	89.1	18.2311673	0.004164896	9.621904247	36.362	0.204
11	1000	12	1.833	0.26	7.892	435.836	4617.846	88.5	12.30441742	0.004584193	9.384074866	35.472	0.199
12	1150	12	0.966	0.221	2.058	46.148	661.064	60.5	1.302839268	0.036800714	8.243592564	31.198	0.192
13	1400	12	0.791	0.246	2.309	5.688	260.374	14.7	0.160582252	0.332377015	5.331588279	20.239	0.655
						Cumulative	e %39Ar rlsd	=	100.0001129		Total gas age =	35.90382	0.1903
Note:	isotope	beams ir	n mV rlsd	= releas	ed, error i	in age inclu	des 0.5% J e	error, all er	rors 1 sigma		no plateau		
(Not c	orrecte	d for deca	av)						-				
APPENDIX C. Continued

Esc24Illite, Illite, 9.48 mg, J = 0.001604 ± 0.5%

4 amu discrimination = $1.01809 \pm 0.17\%$, $40/39K = 0.02207 \pm 129.0\%$, $36/37Ca = 0.0002786 \pm 0.32\%$, $39/37Ca = 0.0006784 \pm 0.43\%$

step	T (C)	t (min.)	36Ar	37Ar	38Ar	39Ar	40Ar	%40Ar*	% 39Ar rlsd	Ca/K	40Ar*/39ArK	Age (Ma)	1s.d.
1	450	12	105.707	0.169	21.111	3.856	34814.9	11.9	0.366031933	0.461001823	1078.017227	1811.269	19.457
2	470	12	20.495	0.047	4.221	9.507	7080.436	16	0.902454768	0.05199408	125.3976634	330.632	3.645
3	510	12	6.373	0.065	1.877	42.774	2781.434	33.6	4.060334517	0.015981897	21.82301334	62.07	0.532
4	540	12	1.907	0.081	1.508	87.932	1746.834	68.8	8.346970934	0.009687954	13.59196575	38.909	0.237
5	565	12	1.146	0.11	1.852	125.186	1975.471	83.6	11.88331783	0.009241253	13.14544122	37.644	0.23
6	585	12	0.829	0.112	1.786	128.008	2055.27	88.8	12.15119701	0.009201844	14.20242799	40.637	0.238
7	610	12	1.008	0.123	2.145	156.303	2533.122	88.8	14.8371082	0.008276212	14.36291265	41.091	0.241
8	630	12	0.927	0.112	1.94	143.189	2299.157	88.7	13.59225789	0.008226255	14.20490211	40.644	0.238
9	665	12	1.186	0.135	2.646	196.371	3101.721	89.2	18.64057487	0.007230197	14.07025289	40.263	0.237
10	705	12	0.868	0.098	1.415	103.545	1679.389	85.6	9.829039546	0.009953848	13.80916394	39.524	0.234
11	770	12	0.736	0.082	0.722	47.547	853.734	76.1	4.513412944	0.018137851	13.47580395	38.58	0.234
12	870	12	0.596	0.0775	0.223	7.989	271.517	38	0.758358172	0.102027055	12.25720692	35.125	0.395
13	1000	12	0.503	0.085	0.111	1.256	159.997	9	0.119226169	0.711893492	10.51643153	30.178	2.815
						Cumulative	e %39Ar rlsd	=	100.0002848		Total gas age =	49.8477	0.2187
Note: isotope beams in mV rlsd = released, error in age includes 0.5% J error, all errors 1 sigma									no plateau				
(Not c	orrecte	ed for dec	av)										

APPENDIX D. U-Pb ISOTOPIC DATA AND AGES

	Isotope ratios					Apparent ages (Ma)						
Grain	Grain	Pb_{c}	U	206Pbm	⁶ Pb _c	²⁰⁶ Pb*	²⁰⁷ Pb*	²⁰⁶ Pb*	²⁰⁷ P	b*	²⁰⁷ P	b*
type	wt.µg	(pg)	(ppm)	²⁰⁴ Pb	⁰⁸ Pb	²³⁸ U	²³⁵ U	²³⁸ U	235	U	²⁰⁶ P	b*
ESC-	1											
1B	32	12	323	1310	6.5	0.023888 ± 0.74	4 0.16966 ± 1.13	152.2 ± 1.	1 159.1 ±	1.6	264 ±	19
1B	21	32	240	79	1.7	0.005815 ± 4.22	2 0.03751 ± 10.70	37.4 ± 1.	6 37.4 ±	3.9	38 ±	220
1Aa	38	23	262	560	6.8	0.019278 ± 0.95	5 0.13388 ± 2.21	123.1 ± 1.	2 127.6 ±	2.6	212 ±	44
1Aa	75	13	196	428	5.2	0.005741 ± 1.75	5 0.03671 ± 3.30	36.9 ± 0.	6 36.6 ±	1.2	17 ±	64
1Aa	51	7	215	543	5.3	0.005782 ± 2.33	3 0.03760 ± 3.19	37.2 ± 0.	9 37.5 ±	1.2	58 ±	50
1Aa	35	12	794	890	7.5	0.005816 ± 1.01	1 0.03671 ± 2.31	37.4 ± 0.	4 36.6 ±	0.8	-14 ±	48
1Aa	32	12	217	232	4.2	0.005798 ± 3.48	3 0.03694 ± 5.31	37.3 ± 1.	3 36.8 ±	2.0	8 ±	92
ESC-	2											
2C	38	8	237	530	4.4	0.007176 ± 2.27	7 0.04881 ± 3.12	46.1 ± 1.	0 48.4 ±	1.4	163 ±	47
1Ba	24	25	134	80	1.5	0.005801 ± 1.77	7 0.03567 ± 12.30	37.3 ± 0.	7 35.6 ±	4.3	-77 ±	280
1Ba	27	36	141	67	1.5	0.005937 ± 2.19	9 0.04212 ± 13.10	38.2 ± 0.	8 41.9 ±	5.3	261 ±	280
1Ba	29	7	629	1020	5.2	0.005821 ± 0.47	7 0.03741 ± 1.90	37.4 ± 0.	2 37.3 ±	0.7	29 ±	42
1Ba	22	11	358	292	4.0	0.005891 ± 0.66	6 0.03789 ± 4.59	37.9 ± 0.	2 37.8 ±	1.7	31 ±	100
1Ba	21	15	895	505	4.3	0.005888 ± 0.56	6 0.03749 ± 2.59	37.8 ± 0.	2 37.4 ±	1.0	7 ±	58
ESC-	4											
5E	22	19	624	413	4.1	0.008436 ± 1.34	4 0.05871 ± 3.01	54.2 ± 0.	7 57.9 ±	1.7	217 ±	59
5E	25	12	630	805	4.9	0.009405 ± 1.10) 0.06377 ± 2.41	60.3 ± 0.	7 62.8 ±	1.5	156 ±	48
1Ba	21	16	593	316	4.0	0.006123 ± 1.90) 0.03977 ± 2.83	39.3 ± 0.	7 39.6 ±	1.1	55 ±	48
1Ba	18	205	1251	139	2.3	0.017231 ± 1.11	1 0.12742 ± 5.30	110.1 ± 1.	2 121.8 ±	6.0	356 ±	110
1Ba	15	5	435	509	5.5	0.006075 ± 3.70	0.03890 ± 4.48	39.0 ± 1.	4 38.7 ±	1.7	21 ±	59
1Ba	19	6	100	143	4.1	0.006164 ± 12.1	10 0.03740 ± 13.10	39.6 ± 4.	8 37.3 ±	4.7	-111 ±	140
1Ba	21	26	229	94	1.8	0.006221 ± 4.21	1 0.03995 ± 8.81	40.0 ± 1.	7 39.8 ±	3.3	27 ±	180
1Ba	20	43	185	125	2.4	0.019325 ± 2.01	1 0.15038 ± 5.15	123.4 ± 2.	5 142.3 ±	5.3	470 ±	99
ESC-	6											
1B	31	7	186	1260	3.9	0.022505 ± 1.23	3 0.16026 ± 1.81	143.5 ± 1.	8 150.9 ±	2.5	270 ±	29
1B	35	7	260	493	5.4	0.005571 ± 2.89	9 0.03590 ± 3.79	35.8 ± 1.	0 35.8 ±	1.4	36 ±	57
1Ba	24	28	425	149	2.9	0.005503 ± 2.46	0.03561 ± 5.56	35.4 ± 0.	9 35.5 ±	2.0	46 ±	110
1Ba	21	12	207	153	1.1	0.005479 ± 5.70	0 0.03570 ± 6.88	35.2 ± 2.	0 35.6 ±	2.5	62 ±	90
1Ba	18	17	170	85	1.9	0.005617 ± 7.14	4 0.03466 ± 11.20	36.1 ± 2.	6 34.6 ±	3.7	-69 ±	200
1Ba	21	9	173	169	3.5	0.005529 ± 6.91	1 0.03593 ± 7.74	35.5 ± 2.	5 35.8 ±	2.7	56 ±	83

APPENDIX D. Continued

Notes: Grain type: A = ~250µ, B = ~200µ, C = ~150µ, D = ~100µ, E = ~80µ, a = abraded in air abrasion device.

Number refers to number of grains analyzed.

²⁰⁶Pb/²⁰⁴Pb is measured ratio, uncorrected for blank, spike, or fractionation.

²⁰⁶Pb/²⁰⁸Pb is corrected for blank, spike, and fractionation.

All uncertainties are at the 95% confidence level.

Uncertainties in isotope ratios are in percent. Uncertainties in ages are in millions of years.

Most concentrations have an uncertainty of 25% due to uncertainty in weight of grain. Constants used:

 238 U/ 235 U = 137.88. Decay constant for 235 U = 9.8485x10⁻¹⁰. Decay constant for 238 U = 1.55125x10⁻¹⁰.

Isotope ratios are adjusted as follows:

(1) Mass dependent corrections factors of: 0.14 ±0.06 %/amu for Pb and 0.04 ±0.04 %/amu for UO2.

(2) Pb ratios corrected for 0.005 ± 0.003 ng blank with ²⁰⁶Pb/²⁰⁴Pb = 18.6 ±0.3, ²⁰⁷Pb/²⁰⁴Pb = 15.5 ±0.3, and ²⁰⁸Pb/²⁰⁴Pb = 38.0 ±0.8.

(3) U has been adjusted for 0.001 ± 0.001 ng blank.

(4) Initial Pb from Stacey and Kramers (1975), with uncertainties of 1.0 for ²⁰⁶Pb/²⁰⁴Pb,

0.3 for ²⁰⁷Pb/²⁰⁴Pb, and 2.0 for ²⁰⁸Pb/²⁰⁴Pb.

All analyses conducted using conventional isotope dilution and thermal ionization mass spectrometry, as described by Gehrels and Boghossian (2000).

APPENDIX E

EQUATIONS USED IN THIS DISSERTATION

Isotope Fractionation Equations

• Oxygen

 $10^{3} ln \alpha_{\text{biotite} - \text{H2O}} = 0.4 \text{ x } 10^{6} \text{T}^{-2} - 3.1; 500^{\circ} \text{ to } 800^{\circ} \text{C};$ Bottinga and Javoy (1973).

 $10^3 \ln \alpha_{\text{illite-muscovite - H2O}} = 2.39 \text{ x } 10^6 \text{T}^{-2} - 3.76; 0^\circ \text{ to } 700^\circ \text{C}; \text{ Sheppard and Gilg (1996).}$

 $10^3 \ln \alpha_{\text{kaolinite} - H2O} = 2.76 \text{ x } 10^6 \text{T}^{-2} - 6.75; 0^\circ \text{ to } 350^\circ \text{C}; \text{ Sheppard and Gilg (1996).}$

• Hydrogen

 $10^3 \ln \alpha_{\text{biotite} - H2O} = -21.3 \times 10^6 \text{T}^{-2} - 2.8$; 400° to 850°C; Suzuoki and Epstein (1976).

 10^{3} ln α_{illite-muscovite - H2O} = 25 ± 5; 120° to 400°C; Sheppard and Gilg (1996). 10³ ln α_{kaolinite - H2O} = 2.76 x 10⁶T⁻² -6.75; 0° to 300°C; Gilg and Sheppard (1996).

Binary Mixing Equation $[1/(1 + x)][C^{A}] + [x/(1 + x)][C^{B}] = C^{mix}$ where x = parts of B in 1 part A, C^A = concentration in rock A, and C^B = concentration in rock B (Rollinson, 1993).

Partial Melting Equations

$$C_{L} = [C_{i}] / [(1-F)(D) + D]$$

Where C_L is concentration of an element in differentiated melt, C_I is concentration of an element in initial melt, F is fraction of liquid remaining, and D is bulk distribution coefficient given D (Rollinson, 1993).

D is the bulk distribution coefficient given by:

 $D = (X_a) (K_d^a) + (X_b) (K_d^b) + (X_c) (K_d^c) + \dots$ where x is the weight fraction of mineral component removed from melt and K_d is solid/liquid distribution coefficient of fractionating phase (Arth, 1976; Green and Pearson, 1985; Dostal et al., 1983; Fujimaki and Hildreth, 1983).

Epsilon Value ()

This value compares ¹⁴³Nd /¹⁴⁴Nd measured with values today (\in°); and values at the time of separation of the melt the formed the rock, where time is known by an independent method (\in ^t) (Rollinson, 1993).

 $\in^{t} = \underbrace{(^{143}\text{Nd}/^{144}\text{Nd})\text{measured} - 1 * 10^{4}}_{^{143}\text{Nd}/^{144}\text{Nd}} \text{ of CHUR at time of melting}$

-Zero is interpreted as melting undepleted mantle. -Negative melting depleted mantle

APPENDIX F

MINERAL ABBREVIATIONS USED IN THIS STUDY

mt = magnetite, bn = bornite, cpy = chalcopyrite, py = pyrite, mo = molybdenite, sp = sphalerite, gn = galena, enar = enargite, tn = tennantite, bt = biotite, garn = grossularite, epid = epidote, kfds = orthoclase, qz = quartz, chl = chlorite, ser = sericite, cal = calcite, hm = hematite, po = pyrrhotite, alu = alunite, wo = wollastonite, anhy = anhydrite, S = sulfur, ol = olivine; grn = garnet of no specific composition, plg = plagioclase, opx = orthopyroxene, cpx = clinopyroxenes, hb = hornblende, and adv. Arg. = advanced argillic.

<u>APPENDIX G</u>	. Micropr	obe Results	<u>. Biotite Co</u>	mposition	Sample Es	<u>(8)</u>
Sample	lgn-1	lgn-1	lgn-1	lgn-1	lgn-1	lgn-1
SiO ₂	38.67	37.09	36.74	36.36	37.15	37.90
TiO ₂	3.49	3.85	3.82	4.44	4.09	3.28
Al ₂ O ₃	15.40	13.72	13.78	13.61	13.94	14.21
FeO⊤	12.58	14.13	12.73	12.58	12.64	13.60
MnO	0.15	0.11	0.12	0.30	0.00	0.14
MgO	14.65	15.95	16.01	15.62	16.00	16.35
CaO	0.16	0.11	0.03	0.01	0.00	0.03
Na ₂ O	0.27	0.30	0.28	0.22	0.19	0.24
K ₂ O	8.02	8.39	9.10	9.18	9.17	7.96
BaO	0.52	0.56	0.13	0.47	0.41	0.30
SrO	0.03	0.02	0.00	0.00	0.00	0.01
ZnO	0.04	0.04	0.00	0.00	0.08	0.03
F	1.04	0.88	0.91	1.07	1.38	0.96
CI	0.20	0.19	0.21	0.21	0.15	0.18
Cr_2O_3	0.01	0.01	0.00	0.04	0.06	0.05
S	0.00	0.00	0.00	0.00	0.02	0.00
V_2O_5	0.27	0.30	0.18	0.14	0.25	0.29
CuO	0.00	0.01	0.00	0.17	0.00	0.01
H ₂ 0	3.19	3.40	3.31	3.13	2.90	3.34
Total	98.68	99.03	97.35	97.55	98.43	98.89
O = F+ Cl	0.48	0.41	0.43	0.50	0.61	0.45
Total	98.19	98.62	96.92	97.06	97.81	98.44
		Cation S	Structural P	ositions		
Si(T)	5.99	5.72	5.72	5.68	5.74	5.83
Aliv(T)	2.01	2.28	2.28	2.32	2.26	2.17
Alvi(M2)	0.80	0.22	0.24	0.19	0.28	0.40
Ti(M2)	0.41	0.45	0.45	0.52	0.48	0.38
Fe3+(M2)	0.00	0.00	0.00	0.00	0.00	0.00
Mg(M2)	3.38	3.67	3.71	3.64	3.68	3.75
Fe2+(M2)	1.63	1.82	1.66	1.64	1.63	1.75
Mn(M2)	0.02	0.01	0.02	0.04	0.00	0.02
Na(M1)	0.08	0.09	80.0	0.07	0.06	0.07
Ca(M1)	0.03	0.02	0.01	0.00	0.00	0.00
K(M1)	1.58	1.65	1.81	1.83	1.81	1.56
	0.03	0.03	0.01	0.03	0.02	0.02
Sr(M1)	0.00	0.00	0.00	0.00	0.00	0.00
F	0.52	0.45	0.47	0.55	0.70	0.49
	0.05	0.05	0.06	0.06	0.04	0.05
5	0.00	0.00	0.00	0.00	0.01	0.00
0H	3.42	3.49	3.47	3.39	3.24	3.40
0	20.00	20.00 End	20.00	∠0.00 Mica	20.00	20.00
X(phl)	0 5/2217			0 603202	0 607124	0 505011
$\chi(pn)$	0.042217	0.004/44	0.011024	0.003202 0 22	0.007 124 0 22	0.00011
	0.23	0.24	0.22	0.23	0.23	0.23
$X(nhl) \cap G/X(nhl)$	0.20 nn\0 22/¥/	sid\0.17	0.10	0.17	0.17	0.17
	····/0.20/A(50,0.17				

APPENDIX G.	Micropro	be Resutl	s. Biotite	Composi	tion (Sam	ple Esc 1)
Sample	Perv-1	Perv-2	Perv-3	Perv-4	Perv-5	Perv-6	Perv-7
SiO ₂	39.03	37.84	36.93	36.04	36.30	37.38	37.93

SiO ₂	39.03	37.84	36.93	36.04	36.30	37.38	37.93			
TiO ₂	3.02	3.27	3.35	3.38	3.47	2.35	3.40			
AI_2O_3	15.04	14.85	15.02	14.75	15.34	15.03	15.70			
FeO⊤	14.48	15.00	13.18	14.96	14.56	16.27	11.45			
MnO	0.16	0.15	0.11	0.29	0.17	0.15	0.12			
MgO	15.34	14.25	14.78	13.52	14.39	12.74	15.90			
CaO	0.01	0.02	0.05	0.02	0.03	0.09	0.03			
Na₂O	0.20	0.12	0.06	0.09	0.14	0.23	0.20			
K₂O	8.91	9.36	8.80	8.92	8.93	9.26	9.38			
BaO	0.14	0.19	0.00	0.34	0.55	0.10	0.00			
SrO	0.31	0.01	0.00	0.00	0.00	0.02	0.00			
ZnO	0.06	0.02	0.00	0.01	0.04	0.04	0.04			
F	0.60	0.66	0.94	0.73	1.31	0.75	1.22			
CI	0.21	0.23	0.21	0.28	0.25	0.23	0.14			
Cr ₂ O ₃	0.02	0.02	0.00	0.02	0.00	0.01	0.00			
S	0.00	0.01	0.00	0.02	0.02	0.00	0.00			
V_2O_5	0.51	0.27	0.17	0.19	0.25	0.29	0.26			
CuO	0.05	0.05	0.00	0.06	0.15	0.04	0.04			
H ₂ 0	3.75	3.57	3.22	3.33	2.83	3.39	3.09			
Total	101.83	99.88	96.84	96.96	98.73	98.37	98.90			
O = F+ Cl	0.30	0.33	0.45	0.37	0.61	0.37	0.55			
Total	101.53	99.55	96.40	96.59	98.12	98.00	98.36			
		Cation	Structura	al Position	ns					
Si(T)	5.86	5.81	5.80	5.72	5.64	5.85	5.78			
Aliv(T)	2.14	2.19	2.20	2.28	2.36	2.15	2.22			
Alvi(M2)	0.52	0.49	0.59	0.48	0.44	0.62	0.60			
Ti(M2)	0.34	0.38	0.40	0.40	0.41	0.28	0.39			
Fe3+(M2)	0.00	0.00	0.00	0.00	0.00	0.00	0.00			
Mg(M2)	3.43	3.26	3.46	3.20	3.33	2.97	3.61			
Fe2+(M2)	1.82	1.93	1.73	1.99	1.89	2.13	1.46			
Mn(M2)	0.02	0.02	0.02	0.04	0.02	0.02	0.02			
Na(M1)	0.06	0.03	0.02	0.03	0.04	0.07	0.06			
Ca(M1)	0.00	0.00	0.01	0.00	0.01	0.01	0.01			
K(M1)	1.71	1.83	1.76	1.81	1.77	1.85	1.82			
Ba(M1)	0.01	0.01	0.00	0.02	0.03	0.01	0.00			
Sr(M1)	0.03	0.00	0.00	0.00	0.00	0.00	0.00			
F	0.30	0.33	0.49	0.38	0.67	0.39	0.61			
CI	0.05	0.06	0.06	0.08	0.07	0.06	0.04			
S	0.00	0.01	0.00	0.02	0.02	0.00	0.00			
OH	3.65	3.60	3.45	3.52	3.24	3.54	3.35			
0	20.00	20.00	20.00	20.00	20.00	20.00	20.00			
		En	d-membe	rs Mica						
X(phl)	0.56	0.54	0.56	0.52	0.55	0.49	0.59			
X(ann)	0.24	0.24	0.21	0.22	0.20	0.25	0.19			
X(sid)	0.20	0.22	0.23	0.25	0.26	0.26	0.22			
X(phl) 0.54/X(ann)0.22/X(sid)0.23										

Sample #	Esc8-1	Esc8-2	Esc8-3	Esc8-4	Esc8-5
SiO ₂	38.77	38.49	41.54	40.23	40.24
TiO	3 49	3 10	1 04	1 34	1.06
	13 02	1/ 10	13 32	14 75	13.00
	10.92	14.10	10.02	14.75	10.01
FeO _T	13.25	13.29	10.08	11.08	10.76
MaO	0.10	0.19	0.11	10.00	0.14
MyO CaO	0.02	0.01	21.32	0.00	20.76
	0.02	0.00	0.03	0.00	0.03
K O	0.24	0.20	7.02	0.27	0.20
	9.11	0.03	7.83	8.79	8.05 0.02
DaU SrO	0.12	0.11	0.00	0.02	0.03
310 7n0	0.01	0.02	0.02	0.02	0.01
F	0.02	0.02	1.60	1.68	1.46
CI	0.00	0.03	0.26	0.27	0.27
Cr_2O_2	0.01	0.01	0.00	0.00	0.01
S	0.00	0.01	0.01	0.01	0.01
V_2O_5	0.33	0.29	0.12	0.16	0.11
CuO	0.00	0.00	0.02	0.00	0.00
H ₂ 0	3.48	3.43	2.71	2.54	2.84
Total	100.25	99.53	100.35	100.09	100.00
O = F+ Cl	0.41	0.42	0.73	0.77	0.67
Total	99.85	99.11	99.62	99.33	99.33
	C	Cation Struct	ural Position	IS	
Si(T)	5.87	5.86	6.09	5.96	5.94
Aliv(T)	2.13	2.14	1.91	2.04	2.06
Alvi(M2)	0.35	0.39	0.39	0.54	0.35
Ti(M2)	0.40	0.35	0.11	0.15	0.12
Fe3+(M2)	0.00	0.00	0.00	0.00	0.00
Mg(M2)	3.67	3.70	4.66	4.17	4.57
$Fe_2+(IVI_2)$	1.68	1.69	1.24	1.37	1.33
Nn(N1)	0.02	0.02	0.01	0.01	0.02
$\operatorname{Na}(\operatorname{IVIT})$	0.07	0.08	0.09	0.08	0.07
K(M1)	1.76	1 72	1.46	0.00	1 51
$R_{a}(M1)$	0.01	0.01	0.00	0.00	0.00
Sr(M1)	0.01	0.01	0.00	0.00	0.00
F	0.00	0.00	0.00	0.82	0.00
	0.05	0.05	0.07	0.02	0.07
S	0.00	0.01	0.01	0.01	0.01
OH	3.51	3.49	3.15	3.10	3.21
0	20.00	20.00	20.00	20.00	20.00
		End-mem	bers Mica		
X(phl)	0.60	0.60	0.73	0.67	0.72
X(ann)	0.26	0.24	0.22	0.20	0.20
X(sid)	0.15	0.16	0.06	0.13	0.09
X(phl) 0.66/X(a	nn)0.22/X(sid)0.12			

APPENDIX G. Microprobe Results. Biotite Composition (Sample Esc 8)

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APPENDIX G.	Micropro	obe Resu	Its. Serici	ite Compo	sitions.	. .		
Sample	Wser1	Wser2	Gser2	Gser3	Gser4	Gser4	Gser5	Gser5
SiO2	48.05	45.64	51.59	48.48	48.33	55.42	52.32	51.21
TiO2	0.18	0.29	0.13	0.16	0.17	0.04	0.48	0.28
AI2O3	35.05	34.09	33.09	33.42	34.41	33.75	34.51	33.85
FeOT	2.05	1.10	2.60	3.37	2.95	2.93	2.52	2.81
MnO	0.00	0.02	0.01	0.07	0.03	0.00	0.00	0.00
MgO	0.90	0.40	1.41	2.30	1.48	1.86	1.99	1.93
CaO	0.09	0.00	0.05	0.00	0.00	0.05	0.10	0.09
Na2O	0.68	0.45	0.12	0.36	0.39	0.17	0.38	0.44
K2O	10.10	8.99	8.03	9.43	8.36	9.11	9.68	9.52
BaO	0.03	0.03	0.18	0.17	0.09	0.09	0.17	0.14
SrO	0.02	0.03	0.02	0.02	0.01	0.00	0.00	0.00
PbO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ZnO	0.01	0.01	0.03	0.01	0.01	0.05	0.03	0.03
F	0.51	0.29	0.23	0.33	0.22	0.21	0.36	0.34
CI	0.02	0.01	0.01	0.03	0.02	0.02	0.03	0.02
Cr2O3	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
NiO	0.00	0.00	0.00	0.00	0.00	0.02	0.01	0.01
P2O5	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.04
S	0.01	0.01	0.03	0.00	0.01	0.02	0.08	0.06
ZrO2	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Y2O3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ce2O3	0.00	0.00	0.00	0.00	0.00	0.07	0.06	0.10
Sc2O3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CoO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
V2O5	0.03	0.05	0.05	0.04	0.07	0.01	0.05	0.07
CuO	0.01	0.00	0.04	0.01	0.02	0.00	0.05	0.04
H20	3.51	3.46	3.84	3.74	3.76	4.12	3.90	3.85
Total	101.24	94.84	101.46	101.93	100.32	107.93	106.77	104.84
O = F+Cl	0.22	0.12	0.10	0.15	0.09	0.09	0.16	0.15
Total	101.02	94.72	101.36	101.79	100.22	107.84	106.62	104.69
Cation Structu	ural Posit	ions						
Si(T)	6.29	6.39	6.83	6.33	6.43	6.89	6.54	6.52
Aliv(T)	1.71	1.61	1.17	1.67	1.57	1.11	1.46	1.48
Alvi(M2)	3.70	4.02	3.99	3.48	3.82	3.84	3.62	3.60
Ti(M2)	0.02	0.03	0.01	0.02	0.02	0.00	0.05	0.03
Fe3+(M2)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg(M2)	0.17	0.08	0.28	0.45	0.29	0.34	0.37	0.37
Fe2+(M2)	0.22	0.13	0.29	0.37	0.33	0.30	0.26	0.30
Mn(M2)	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Na(M1)	0.17	0.12	0.03	0.09	0.10	0.04	0.09	0.11
Ca(M1)	0.01	0.00	0.01	0.00	0.00	0.01	0.01	0.01
K(M1)	1.69	1.61	1.36	1.57	1.42	1.44	1.54	1.55
Ba(M1)	0.00	0.00	0.01	0.01	0.00	0.00	0.01	0.01
Sr(M1)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
F	0.23	0.14	0.10	0.15	0.10	0.09	0.15	0.15
CI	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.01
S	0.01	0.00	0.02	0.00	0.01	0.01	0.06	0.05
ОН	3.76	3.86	3.87	3.84	3.89	3.90	3.78	3.80
0	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00

Sample location in Appendix A. Gser = Dark Sericite; Wser = White Sericite.

Sample	Esc 8-ilme	Esc 9mt	Esc 9mt	Esc 9mt	Esc 9mt	Esc 9-ilme	Esc 9-ilme	Esc 9-ilme
SiO2	0.03	0.01	0.05	0.08	0.12	0.05	0.05	29.17
TiO2	21.30	1.63	0.51	0.26	0.47	46.11	19.68	0.84
Al2O3	0.06	0.33	0.10	0.12	0.08	0.03	0.12	18.30
FeO⊤	67.26	83.56	91.35	86.21	86.71	45.12	67.64	19.37
MnO	0.10	0.08	0.09	0.00	0.16	0.01	0.62	0.29
MgO	0.06	0.01	0.00	0.00	0.00	0.00	0.00	20.06
CaO	0.17	0.00	0.02	0.02	0.04	0.09	0.05	0.15
Na2O	0.06	0.00	0.02	0.00	0.07	0.00	0.02	0.07
K2O	0.04	0.00	0.00	0.00	0.07	0.02	0.00	0.02
BaO	0.00	0.00	0.00	0.06	0.06	0.35	0.00	0.00
SrO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
ZnO	0.00	0.06	0.01	0.22	0.05	0.00	0.01	0.07
F	0.23	0.00	0.00	0.00	0.00	0.00	0.03	0.15
CI	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.01
Cr2O3	0.00	0.00	0.06	0.18	0.00	0.03	0.13	0.02
S	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.01
V2O5	1.49	0.48	0.63	0.63	0.62	1.93	1.52	0.23
CuO	0.13	0.05	0.02	0.13	0.36	0.01	0.00	0.13
H20	-1.26	0.00	-0.01	-0.04	0.00	-0.07	-0.19	-1.37
Total	89.66	86.21	92.85	87.91	88.79	93.70	89.68	87.53
O = F+Cl	0.10	0.00	0.00	0.00	0.00	0.00	0.01	0.06
Total	89.56	86.21	92.85	87.91	88.79	93.70	89.67	87.46
			Cation	Structura	al Positic	ons		
Si(T)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.59
Aliv(T)	0.00	0.02	0.00	0.01	0.00	0.00	0.00	0.44
Alvi(M2)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr(M2)	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Fe3+(M2)	0.58	1.84	1.91	1.91	1.92	0.02	1.10	0.34
V(M2)	0.04	0.01	0.02	0.02	0.02	0.03	0.03	0.00
Mg(M1)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.61
Ti(M1)	0.65	0.05	0.01	0.01	0.01	0.94	0.40	0.01
Fe2+(M1)	1.70	1.07	1.04	1.04	1.01	1.00	0.44	0.00
Mn(M1)	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.01
Ca(M1)						0.00	0.00	0.00
Ba(M1)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sr(M1)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
F	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.01
CI	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
OH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0	3.97	4.00	4.00	3.99	4.00	3.00	3.00	2.99
Magnetite	-Ilmenite P	airs: Spe	encer an	d Lindsle	ey (1981)), and Stori	mer (1983)	
	T(°C)	logfO2			T(°C)	logfO2		
Ign	458	-30.2		Perv	631	-13.7		
Ign	u 429	-31.0		Perv	668	-12.9		

APPENDIX G. Microprobe Results. Magnetite-ilmenite Compositions (Sam. Esc 8, Esc 9)

Sample location in Appendix A. mt = magnetite; ilm = ilmenite

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