Economic Geology
Vol. 91, 1996, pp. 164–179

Age of Supergene Oxidation and Enrichment in the Chilean Porphyry Copper Province

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Abstract

Twenty-five samples of supergene alunite collected from deeply developed supergene profiles in porphyry copper deposits and prospects between latitudes 20° and 27° S in northern Chile yield K/Ar ages ranging from about 34 to 14 Ma. Therefore supergene oxidation and enrichment processes were active from the early Oligocene to the middle Miocene, a minimum of 20 m.y. Supergene activity at individual deposits lasted for at least 0.4 to 6.2 m.y. The early Oligocene supergene activity affected deposits in the Paleocene porphyry copper belt, whereas early and middle Miocene supergene processes are documented in the Early Cretaceous, Paleocene, and late Eocene to early Oligocene porphyry copper belts. Middle Miocene oxidation also affected the oldest epithermal gold-silver deposits in the Maricunga belt farther east. Supergene activity commenced no less than 11 m.y. after generation of each porphyry copper deposit because of the time required to unroof the copper-bearing parts of the system. Supergene activity throughout northern Chile ceased at ~14 Ma. The geologic features of deposits and prospects and their morphotectonic positions, present latitudes, and present elevations display no obvious correlations with the supergene chronology.

Exploration for major cumulative enrichment blankets should not be carried out either beneath thick sequences of piedmont gravels (± ignimbrites) of Oligocene through middle Miocene age unless their accumulation is demonstrably late in the documented history of supergene activity, or in porphyry copper provinces, such as those of central Chile and northwestern Argentina, which formed after ~14 Ma.

The uplift responsible for efficient cumulative copper enrichment is difficult to correlate convincingly with the brief pulses of compressive tectonism postulated for northern Chile and contiguous areas unless their effects were much more prolonged. Intensifying aridity is confirmed as the likely reason for the cessation of supergene activity in northern Chile, and tectonic uplift was its most probable cause. However, more fundamental global controls producing a period of chemical weathering followed by worldwide dessication also may have played a role.

Introduction

SUPERGENE oxidation and leaching, commonly giving rise to underlying chalcocite enrichment (e.g., Emmons, 1917), are important processes that affected the uppermost several hundred meters of the 12 major porphyry copper deposits in northern Chile (Sillitoe, 1990; Fig. 1), and are the principal reason for the economic pre-eminence of the Chilean copper province. Indeed, perhaps only two of these major deposits (Chuquicamata and MM) would be commercially viable if enriched and/or oxidized zones had not developed.

A middle Tertiary age was suggested half a century ago for supergene sulfide enrichment at the Chuquicamata (Taylor, 1935; Bandy, 1938; Jarrell, 1944) and Potrerillos (March, 1935) porphyry copper deposits in northern Chile (Fig. 1). However, this overall timing for oxidation and enrichment was not confirmed until about 30 years later, when K-Ar ages as old as about 13 Ma were obtained for ignimbrite flows capping pedimented surfaces which truncated the supergene profiles developed over copper deposits between latitudes 26° and 28° S (Sillitoe et al., 1968). Geomorphologic history, constrained by radiometric dating of volcanic rocks, was also used to suggest that supergene oxidation and enrichment took place at Chuquicamata, and probably elsewhere in northern Chile, during the late Oligocene to early Miocene interval (Mortimer et al., 1977). The same approach was also employed for dating the supergene oxidation and enrichment of porphyry copper deposits in southwestern North America (Livingston et al., 1968) and in southern Peru (Clark et al., 1990). The middle Tertiary timing for enrichment in northern Chile was substantiated further by Alpers and Brimhall (1988), who obtained K-Ar ages of 18 ± 0.7 to 14.7 ± 0.5 Ma for supergene alunite from the Escondida porphyry copper deposit (Fig. 1).

Alunite is a relatively common mineral in supergene profiles (e.g., Emmons, 1917; Anderson, 1982) and has been dated successfully using both the K/Ar and $^{40}Ar/^{39}Ar$ techniques. Supergene alunite ages constrain the timing of oxidation at several gold deposits, including breccia-hosted ones in Queensland, Australia (Bird et al.,1990), and sediment-hosted (Bloomstein et al., 1990; Sillitoe and Bonham, 1990; Arehart et al., 1992) and epithermal (Ashley and Silberman, 1976; Tingley and Berger, 1985; Sander, 1988; Arehart and O'Neil, 1993; Sillitoe and Lorson, 1994; Vasconcelos et al., 1994) types in Nevada. Radiometric ages for supergene alunite from porphyry copper deposits have not been reported, however, except for those mentioned above for Escondida (Alpers, 1986; Alpers and Brimhall, 1988) and two from El Salvador (Gustafson and Hunt, 1975) in northern Chile (Fig. 1).

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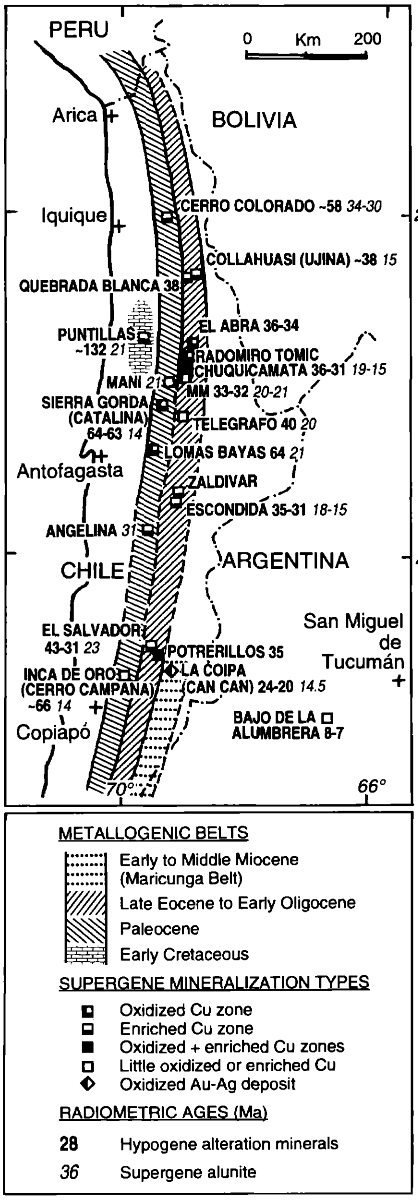

FIG. 1. Map showing porphyry copper deposits and prospects included in this study along with other major porphyry copper deposits in northern Chile and northwestern Argentina. Boundaries of metallogenic belts are illustrative only and taken from Sillitoe (1988). Ages of hypogene alteration-mineralization are taken from the following: the summary by Sillitoe (1988), which may be consulted for original data sources, Maksaev et al. (1988), E.H. McKee and R.H. Sillitoe (unpub. data), and C. Mpodozis (pers. commun., 1994). Ages of supergene alunite, approximated to the nearest 0.5 m.y., are from this study (Table 1) and, for Escondida, Alpers (1986).

This paper reports 21 new K/Ar ages for supergene alunite from porphyry copper deposits and prospects throughout northern Chile. The study was carried out to confirm that all supergene oxidation and enrichment in northern Chile took place during the middle Tertiary, to provide more information on the duration of the oxidation and enrichment event, and to assess the roles of deposit size and hypogene grade, age of hypogene mineralization, and geomorphologic setting in controlling any age differences detected. Finally, consideration is given to the implications of the results for both porphyry copper exploration and the fundamental controls of the oxidation and enrichment event.

Regional Setting

Metallogenic framework

The porphyry copper deposits and prospects selected for sampling are located in northern Chile between latitudes 20° and 27° S (Fig. 1). All these deposits and prospects may be assigned to three discrete, north-trending porphyry copper belts defined using the available geochronologic data for ages of intrusion and hypogene alteration and mineralization (Maksaev et al., 1988; Sillitoe, 1988; Boric et al., 1990). The three belts become progressively younger eastward, from Early Cretaceous (~130 Ma) through Paleocene (66-58 Ma) to late Eocene to early Oligocene (42-31 Ma; Fig. 1), as do all igneous and metallogenic belts in northern Chile (e.g., Farrar et al., 1970; Sillitoe, 1972; Boric et al., 1990; Mpodozis and Ramos, 1990).

The late Eocene to early Oligocene belt is the principal repository of copper in the world, and far outweighs the two belts farther west in economic importance. The belt contains major producing deposits at Quebrada Blanca, Chuquicamata, Zaldívar, Escondida, and El Salvador, as well as the Collahuasi (Rosario and Ujina), El Abra, Radomiro Tomic, and MM deposits, all currently at or beyond the feasibility stage (Fig. 1). The Potrerillos deposit, at the southern end of the belt, ceased formal production in 1959. In contrast, the Paleocene belt contains only Cerro Colorado, which began production in 1994, the Sierra Gorda district, where Catalina is at the feasibility stage, and the small producing deposit at Lomas Bayas (Fig. 1). There is no significant copper production from the Early Cretaceous belt.

Most of the major porphyry copper deposits in the Paleocene and late Eocene to early Oligocene belts are characterized by the volumetrically important development of pyrite-rich, sericitic alteration, generally superimposed on earlier K silicate assemblages containing appreciably lower hypogene sulfide contents (e.g., Gustafson and Hunt, 1975; Hunt et al., 1983; Alvarez and Flores, 1985; Hunt, 1985; Ojeda, 1990; Maturana and Saric, 1991). Much of the deep supergene leaching and enrichment of copper in these deposits is attributed to the high acid-generating and low neutralizing capacities of the quartz-sericite-pyrite alteration assemblage (Fig. 2).

Furthermore, meter-scale massive sulfide veins, with similarities to those at Butte, Montana, are late-stage overprints to several deposits, especially in the late Eocene to early Oligocene belt (e.g., Alvarez and Flores, 1985; Hunt, 1985; Sillitoe et al., 1994). These veins possess wide sericitic and/or advanced argillic (quartz-pyrophyllite or quartz-alunite) alteration halos (Fig. 2) and contain abundant pyrite plus hypogene bornite, enargite, chalcocite, and/or covellite. Sillitoe (1991) proposed that these Butte-type veins are the roots to extensive, grossly tabular zones of advanced argillic alteration (lithocaps), one of which is still preserved above the El Salvador deposit (Gustafson and Hunt, 1975). These

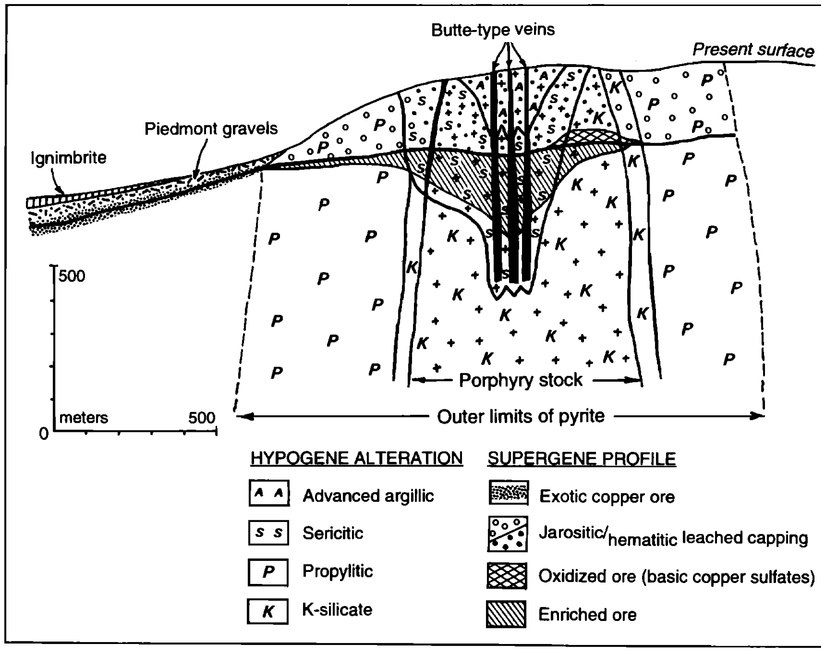

FIG. 2. Idealized hypogene alteration pattern and supergene profile for a typical porphyry copper deposit in northern Chile. Enrichment is believed to have been promoted by the high pyrite content and low neutralizing capacity characteristic of the basal parts of the advanced argillic zone and the underlying sericitic zone, especially where steep, Butte-type veins are present (see text). Note the variation in type of leached capping above the water table (redox boundary). Exotic oxide copper mineralization is shown at the unconformable contact between bedrock and piedmont gravels beyond the pyrite front.

veins are subject to supergene leaching and concomitant sulfide enrichment for the same reasons as those mentioned for the pyrite-rich sericitic alteration; they also provided steep structures that allowed extended downward percolation of supergene solutions (Fig. 2). Indeed, such veins facilitated appreciable sulfide enrichment to depths of >600 m in the Chuquicamata deposit (Alvarez et al., 1980; Flores, 1985).

In contrast, major porphyry copper deposits dominated by K silicate alteration and deficient in pyrite-rich sericitic alteration, such as El Abra (Ambrus, 1977) and Radomiro Tomic, both in the late Eocene to early Oligocene belt (Fig. 1), are characterized largely by in situ oxidation of their hypogene sulfides and, consequently, only weakly developed enrichment.

The Puntillas porphyry copper prospect defines the Early Cretaceous belt in the study area and Telégrafo is late Eocene (Fig. 1), whereas the other three prospects sampled (Maní, Angelina, La Cerro Campana), none of which has been dated radiometrically, are assigned to the Paleocene belt on the basis of their locations (Fig. 1). K silicate and sericitic alteration are both mapped at these prospects and, at Angelina and Cerro Campana, the remnants of advanced argillic alteration zones are also preserved. Copper mineralization is developed only weakly, except at Telégrafo and possibly Angelina.

The Maricunga gold belt, comprising porphyry gold-(copper) deposits and higher level zones of advanced argillic alteration containing high sulfidation (acid sulfate), epithermal gold-silver mineralization, lies immediately south and east of the southern end of the late Eocene to early Oligocene porphyry copper belt (Vila and Sillitoe, 1991; Fig. 1). The Maricunga belt is latest Oligocene to late Miocene (25-6 Ma; Sillitoe et al., 1991; McKee et al., 1994; Mpodozis et al., 1994) in age, and therefore continues the progressive eastward younging defined by the three porphyry copper belts farther west (Sillitoe et al., 1991; McKee et al., 1994). Supergene alunite is scarce in the Maricunga belt, but was collected from one locality, Can Can in the La Coipa district, for comparative purposes.

Geomorphologic framework

Northern Chile is characterized by four main longitudinal morphotectonic-physiographic provinces from the Pacific coast eastward: Coastal Cordillera, Longitudinal Valley, Precordillera, and Andean Cordillera (Fig. 3). Preandean basins separate the Precordillera and Andean Cordillera in places (Fig. 3). Most of the region has a desert climate and lacks vegetation, although precipitation increases progressively eastward with elevation and becomes sufficient to support a sparse, xerophytic flora at >3,000 m above sea level. Hyperaridity (say, <50 mm/yr precipitation) affects the Coastal Cordillera, Longitudinal Valley, and western Precordillera, but annual precipitation attains 100 to 200 mm at the Collahuasi deposit on the eastern edge of the Precordillera (4,800 m a.s.l., Fig. 3; Fuenzalida, 1966; De Beer and Dick, 1994).

Much of northern Chile displays a mature landscape, the "matureland" of Segerstrom (1963), typified by rounded, colluvium-veneered hills and mountains grading to piedmont gravel-filled depressions. The Longitudinal Valley lacks bed-

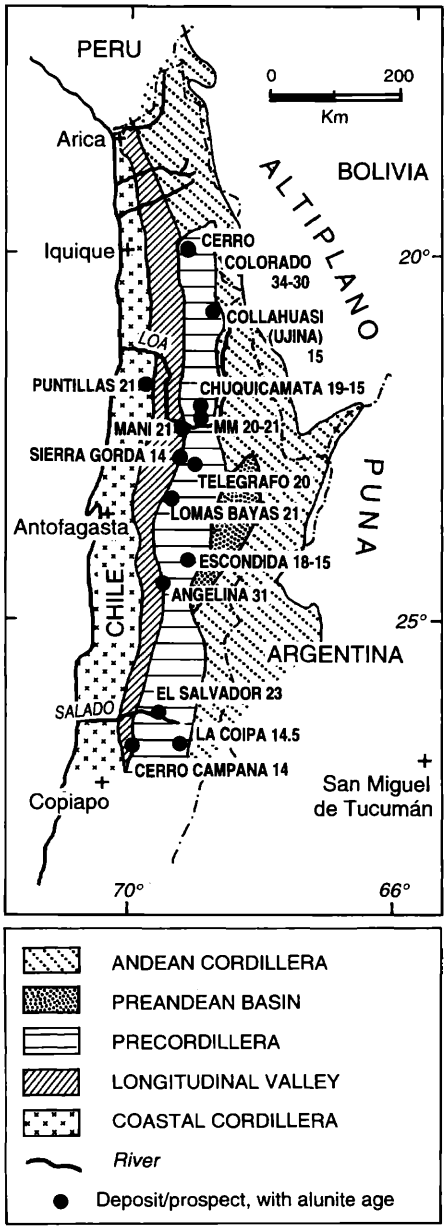

FIG. 3. Map showing porphyry copper deposits and prospects for which supergene alunite ages have been obtained in relation to the morphotectonic provinces of northern Chile. Alunite ages, approximated to the nearest 0.5 m.y., are from this study (Table 1) and, for Escondida, Alpers (1986). The Salar de Atacama occupies the northern part of the Preandean basin.

rock outcrops north of latitude 22° S and is filled in places by as much as 900 m of Oligocene and younger sedimentary and volcanic materials (Mordojovic, 1965). Galli-Olivier (1967), Mortimer et al. (1974), Mortimer and Saric (1975), and Naranjo and Paskoff (1985) recognized that much of northern Chile represents a series of uplifted and variably dissected pediplain surfaces developed across a variety of rocks. Both Oligocene and middle Miocene pediplains are readily distinguishable, the former best preserved in the Coastal Cordillera north of latitude 24° S (Mortimer and Saric, 1975) and the latter, the Atacama pediplain (Sillitoe et al., 1968), dominating south of about latitude 26° S (Mortimer, 1973).

Galli-Olivier (1967), Mortimer and Saric (1975), and Naranjo and Paskoff (1985) appreciated that the middle Tertiary pediplanation of northern Chile took place under more pluvial, but probably semiarid conditions (say, ~300 mm/yr precipitation), which accords with Brüggen's (1950) concept of climatic dessication of the region starting at the beginning of the Oligocene. This concept is supported by the existence of evaporitic salt in the San Pedro Formation (Brüggen, 1934), of Oligocene age (Naranjo et al., 1994), west of the Salar de Atacama (Fig. 3).

Ignimbrite flows derived from calderas in the Andean Cordillera provide a minimum age of ~24 Ma for the initial deposition of the main piedmont gravel sequences along the western border of the Precordillera at latitudes 19° to 21° S (e.g., Naranjo and Paskoff, 1985); however, gravel aggradation farther south (e.g., latitudes 26°–27° S) may not have commenced until about 17 Ma (C. Mpodozis, written commun., 1995). Since ~14 Ma, aridity has intensified in northern Chile (Mortimer and Saric, 1975; Alpers and Brimhall, 1988; this paper), and the landscape as far east as the Precordillera has become largely fossilized except for the incision of transverse valleys by exorheic rivers, the Loa and Salado in the study area (Fig. 3). South of the Salado valley, there is progressive erosional dissection of the Atacama pediplain as a consequence of greater post-14 Ma precipitation.

Supergene oxidation and enrichment generally are believed to have taken place before and during development of the composite pediplain in northern Chile (Sillitoe et al., 1968; Mortimer, 1973; Alpers and Brimhall, 1988). In fact, supergene profiles at several deposits became either partially (e.g., Cerro Colorado, Escondida) or even completely (e.g., Ujina at Collahuasi, MM, Radomiro Tomic) concealed beneath piedmont gravels and/or ignimbrite flows that accumulated before and during the Atacama pedimentation event.

Following extreme climatic dessication and cessation of supergene activity in the western parts of northern Chile, the middle Tertiary oxidation and enrichment profiles were fossilized and capped by sulfate-rich crusts developed by capillary action as cements to both near-surface bedrock and piedmont gravels. The nitrate and associated iodine deposits of northern Chile are facies of these sulfatic accumulations (Ericksen, 1981).

Supergene Setting

Alunite characteristics and occurrence

Alunite of supergene origin was described from oxidized ore at the Chuquicamata porphyry copper deposit by Lindgren (1917), Bandy (1938), and Jarrell (1944) and has been reported more recently from El Salvador (Gustafson and Hunt, 1975) and Escondida (Alpers, 1986; Alpers and Brimhall, 1988). However, despite its widespread distribution and local abundance in supergene profiles developed throughout the porphyry copper province of northern Chile, supergene alunite is still not recognized commonly because of its drab, nondescript appearance and frequent occurrence in waste rock rather than in ore. Supergene alunite is far more abundant in northern Chile than in more humid regions, such as the western Pacific region, probably because aridity results in less dilution of supergene solutions and hence lower pH values and greater sulfate activities. Furthermore, evaporative concentration of supergene solutions may have played an important role in supergene alunite formation in northern Chile, as it did in hypersaline lakes in Australia (Long et al., 1992).

Supergene alunite in the porphyry copper deposits and prospects of northern Chile, like that elsewhere (e.g., Arehart et al., 1992; Sillitoe, 1993), is characteristically massive, cryptocrystalline, and porcelaneous in aspect. Its hardness of 5 may result in confusion with chalcedonic quartz-kaolinite mixtures or "silicified kaolinite." The supergene alunite, commonly approaching the potassium end-member composition (A.J.B. Thompson and E.U. Petersen, unpub. data), displays one of a range of colors: white through cream, buff, tan, yellow, and red to olive green in oxidized zones, but only white and cream in sulfide enrichment zones. Substitution of Fe^{3+} and Cu^{2+} for some of the Al^{3+} in the alunite structure gives rise to the yellow and green colorations, respectively (Scott, 1987; Alpers et al., 1992). However, admixture with or partial replacement by jarosite produces a similar yellowish hue and cannot be distinguished readily in hand samples from the effect of the Fe^{3+} substitution. Olive-green alunite is commonplace in the oxidized zone at Chuquicamata, and samples collected during this study contain as much as 0.58 percent Cu (A.J.B. Thompson and E.U. Petersen, unpub. data). The red alunite is probably attributable to admixed hematite.

Alunite most commonly occupies well-defined but irregularly distributed veinlets, ranging from a few millimeters to as much as 3 cm or more in width, which invariably cut all hypogene veinlets and mineralized fractures developed in the porphyry copper systems (Fig. 4). The alunite veinlets cut copper ore and barren rock alike and are generally monomineralic, although kaolinite, apparently also of supergene origin, is present locally. At the Chuquicamata deposit, some of the alunite occupies the same veinlets as, and is interbanded with, a fibrous basic copper sulfate, antlerite (cf. Bandy, 1938). Near-surface veinlets filled with alkali sulfate and nitrate minerals, at Sierra Gorda (Catalina) and Maní, are the only structures observed to cut alunite veinlets, in keeping with the relative timing of supergene oxidation and nitrate development noted above. The alunite also occurs, although less commonly, as a pervasive replacement of plagioclase crystals in porphyries and volcanics resulting in hard, porcelaneous rocks of siliceous aspect.

The diagnostic appearance and textural relations of supergene alunite distinguish it from alunite of hypogene origin developed as a component of advanced argillic alteration, in either the high sulfidation (acid sulfate) epithermal-lithocap setting or the steam-heated environment above paleowater tables (e.g., Sillitoe, 1993). In fact, supergene alunite is normally absent from advanced argillic alteration zones because of the lack of minerals susceptible to supergene acid attack. Nevertheless, supergene alunite may be present within meters of advanced argillic alteration, as at MM, Cerro La Campana, and La Coipa. Supergene alunite also may be distinguished from the hypogene varieties using sulfur, oxygen, and hydrogen isotope studies (e.g., Rye et al., 1992), but only the first of these isotopic systems has been applied to confirm the supergene origin of alunite samples from northern Chile (Alpers and Brimhall, 1988). Furthermore, the existence of large age gaps between alunite and older, demonstrably hypogene alteration minerals, as documented in this study, is also evidence favoring a supergene origin (cf. Rye et al., 1992).

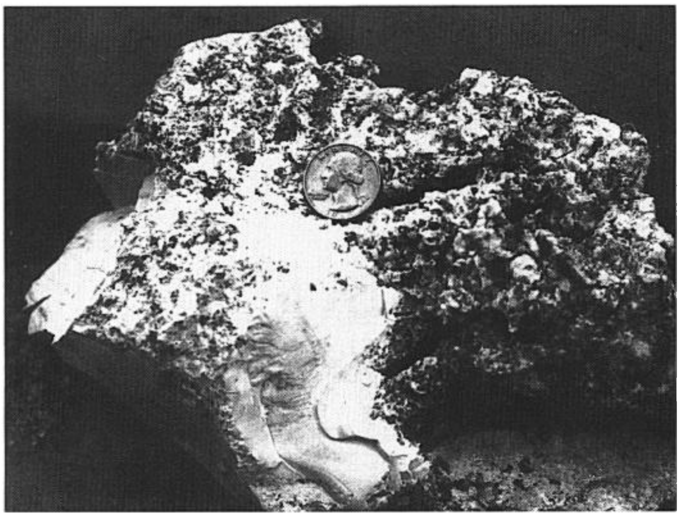

FIG. 4. Typical veinlet of white, massive, monomineralic, supergene alunite cutting weakly sericitized or propylitized rocks subjected to supergene kaolinization in porphyry copper systems, northern Chile. The alunite formed when pyrite was oxidized and so provides a minimum age for the oxidation (and any accompanying sulfide enrichment) event. Coin, 2 cm across, for scale.

Alunite-bearing supergene profiles

Alunite is generated under acidic conditions (Hemley et al., 1969) and, as a consequence, may develop in supergene profiles only at and beneath places where abundant pyrite is undergoing oxidation (e.g., Bladh, 1982; Nordstrom, 1982). In fact, alunite formation ceases once pyrite oxidation is complete (Ague and Brimhall, 1989). Therefore, supergene alunite in the porphyry copper systems of northern Chile is most abundant in or beneath leached cappings dominated by jarosite or hematite which, following Anderson (1982), generally are the oxidation products of sulfide zones rich in pyrite and pyrite-chalcocite mixtures, respectively. Where chalcocite/pyrite ratios are high, oxidation gives rise to the basic copper sulfates, brochantite and antlerite, as well as hematite and alunite, as observed at Chuquicamata. Indeed, the intimate association of alunite, some of it olive green, and antlerite in the oxidized zone at Chuquicamata (see above) is taken as confirmation that alunite formed in oxidized zones and is not the result of inheritance from precursor sulfide enrichment blankets (Alpers and Brimhall, 1988).

Supergene alunite also forms, although apparently less commonly in northern Chile, in the sulfide zones underlying jarositic and hematitic leached cappings. Sulfide zones beneath jarositic leached cappings in northern Chile commonly contain only minor amounts of chalcocite, whereas those beneath hematitic leached cappings constitute cumulative or multicyclic enrichment blankets (cf. Anderson, 1982). In the zone of Butte-type veins at Chuquicamata, supergene alunite veinlets persist to depths of 1,000 m.

In northern Chile, supergene alunite was collected from jarositic leached cappings at Cerro Colorado, MM, Sierra Gorda (Catalina), Lomas Bayas, Maní, Telégrafo, El Salvador, and Cerro La Campana (Fig. 5; Table 1). At several of these localities, the jarositic zone sampled is peripheral to either oxidized copper ore (Sierra Gorda, Lomas Bayas) or protore (Telégrafo) accompanied by goethitic or mixed limonites, or to hematitic leached cappings above enriched sulfide ore (Cerro Colorado, El Salvador). Hematitic leached cappings yielded the supergene alunites from Ujina (Collahuasi), Puntillas, Chuquicamata, and Angelina, and one of the samples from Chuquicamata is from hematitic antlerite ore (Fig. 5; Table 1). Only two alunite samples, from Cerro Colorado and Chuquicamata (Fig. 5; Table 1), were collected from sulfide enrichment blankets.

Oxidized zones characterized by goethite, atacamite (basic copper chloride), and chrysocolla (Fig. 5), like those constituting major orebodies at El Abra and Radomiro Tomic (Fig. 1), developed by transformation essentially in situ of pyrite-poor, chalcopyrite ± bornite mineralization. The low acid production during development of such zones precludes the precipitation of appreciable quantities of alunite.

Sampling and Analysis

Sampling procedures

All alunite samples were collected from crosscutting, monomineralic veinlets not less than about 1 cm wide. The material for analysis was taken exclusively from the central parts of the veinlets in order to avoid contamination by potassium-bearing hypogene alteration products, particularly sericite, in adjoining wall rocks. Because large alunite samples are readily available, the elaborate analytical techniques required when only small quantities of material are present (e.g., Vasconcelos et al., 1994) are not required. None of the veinlets sampled shows any evidence for reopening or replacement by later generations of alunite; hence, single discrete supergene events are believed to have been dated in all cases.

The project began with a pilot study at the Chuquicamata deposit as a means of assessing the reliability of the K-Ar ages determined for supergene alunite. Six samples collected from different parts of the 4- × 1.8-km open pit over approximately 200 vertical meters of supergene profile yielded seven ages of 19.0 ± 0.7, 18.1 ± 0.7, 17.6 ± 0.6, 16.8 ± 1.2, 16.5 ± 0.5, 16.3 ± 0.6, and 15.2 ± 0.5 Ma (Table 1). These ages represent an interval of 2.6 to 5.0 m.y. when account is taken of the analytical uncertainties. This relatively tight grouping of the ages is interpreted to confirm the effectiveness of the sampling (and analytical) techniques employed, as well as the suitability of supergene alunite for K/Ar dating. The limited spread of the ages suggests that neither random argon loss from alunite by diffusion nor potassium exchange with younger supergene solutions is a serious problem (cf. Vasconcelos et al., 1994). If the ages represented reequilibration

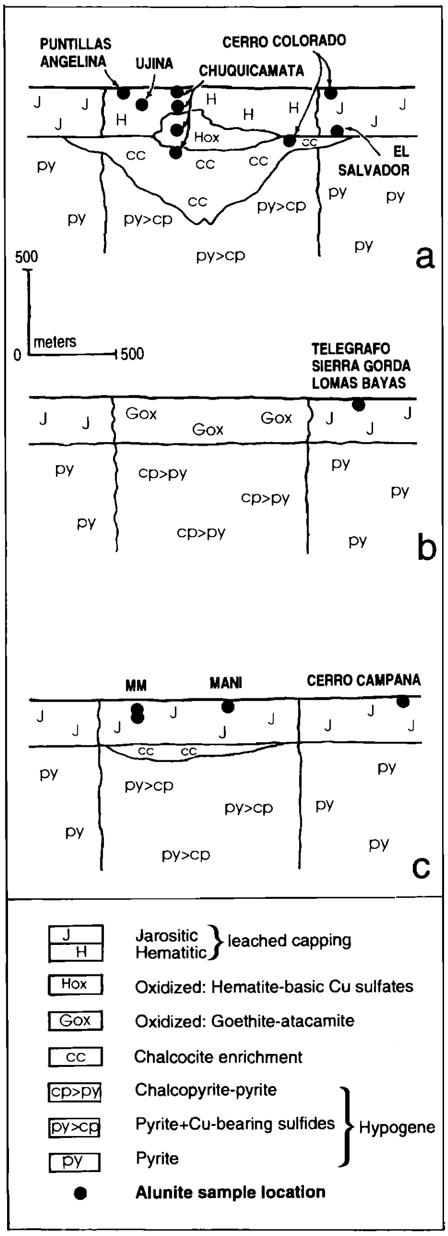

FIG. 5. Schematic representation of alunite sample sites with respect to supergene profiles developed over porphyry copper deposits and prospects, northern Chile. a. Hematitic leached capping underlain by an irregular oxidized zone rich in basic copper sulfates, a cumulative enrichment blanket, and pyritic hypogene ore-protore. b. Goethitic leached capping with various amounts of oxidized copper minerals, chiefly atacamite, underlain by pyrite-deficient, hypogene chalcopyrite ± bornite ore-protore. c. Jarositic leached capping underlain by only minor chalcocite enrichment and pyritic protore.

of early formed alunite with younger supergene solutions, a much broader range of ages than that observed would be expected. This conclusion gains additional support from the similarities of the ages determined for alunite pairs from different parts of the MM (20.8 ± 0.6 and 20.4 ± 0.6 Ma) and Cerro Colorado (34.3 ± 1.1 and 30.3 ± 1.1 Ma) deposits (Table 1). If it is accepted that alunite which formed up to hundreds of meters apart, both vertically and horizontally, is

TABLE 1. K/Ar Ages of Supergene Alunite Samples from Northern Chile

Sample no.	Deposit/prospect	Location details	Latitude/longitude	Hypogene setting	Supergene setting	K_2O (%)	$^{40}Ar^*$ (mole/g $\times 10^{-10}$)	$^{40}Ar^*/\Sigma^{40}Ar$ (%)	Age $\pm \sigma$ (Ma)
COD-93-15	Cerro Colorado	Summit of Cerro Colorado (2,625 m)	20°02′36″/69°17′17″	Sericitic hydrothermal breccia	Jarositic leached capping	6.52	3.2469	48.2	34.3 ± 1.1
COD-93-17	Cerro Colorado	Open pit, 2,550-m level	20°02′44″/69°16′53″	Sericitic hydrothermal breccia	Top of enrichment blanket	8.03	3.5347	33.8	30.3 ± 1.1
COD-93-14	Collahuasi (Ujina)	Exploration shaft, 90-92 m	20°59′46″/68°38′18″	Sericitic rhyolite	Hematitic leached capping	10.24	2.2334	67.7	15.2 ± 0.5
COD-93-5	Puntillas	Surface pit	21°55′40″/69°42′50″	Sericitic rhyodacite porphyry	Hematitic leached capping	5.91	1.8026	23.3	21.1 ± 0.6
COD-91-2	Chuquicamata	South of open pit, bench G-2	22°17′40″/68°54′00″	Sericitic porphyry	Hematitic leached capping near top of enrichment	8.61	2.0277	22.5	16.3 ± 0.6
COD-91-4	Chuquicamata	North of open pit, bench C-4	22°16′03″/68°53′35″	Sericitic prophyry	Hematitic leached capping ~50 m below surface	7.37	2.0152	45.7	19.0 ± 0.7
COD-91-6	Chuquicamata	North of open pit, bench D-4	22°16′11″/68°53′47″	Sericitic porphyry	Hematitic leached capping ~85 m below surface	9.68	2.3144	79.1	16.5 ± 0.5
COD-91-7	Chuquicamata	North of open cut, bench D-4	22°16′11″/68°53′47″	Sericitic porphyry	Antlerite ore ~100 m below surface	8.82	2.3106	64.1	18.1 ± 0.7
COD-91-7b	Chuquicamata	North of open pit, bench D-4	22°16′11″/68°53′47″	Sericitic porphyry	Antlerite ore ~100 m below surface	8.89	2.2607	57.8	17.6 ± 0.6
COD-91-8	Chuquicamata	North of open pit, bench D-4	22°16′11″/68°53′47″	Sericitic porphyry	Top of enrichment blanket	6.77	1.4893	23.8	15.2 ± 0.5
COD-92-9	Chuquicamata	South of open pit, bench G-3	22°16′25″/68°53′59″	Gouge in West fault	Hematitic leached capping	2.114	0.5144	7.14	16.8 ± 1.2
COD-92-7	MM (Central body)	Exploration shaft, 55 m	22°22′32″/68°54′44″	Sericitic granodiorite	Jarositic leached capping	3.09	0.9139	45.7	20.4 ± 0.6
COD-92-8	MM (Central body)	Exploration shaft, 93 m	22°22′32″/68°54′44″	Sericitic granodiorite	Jarositic leached capping	7.09	2.1325	70.5	20.8 ± 0.6
COD-92-4	Maní	Surface	22°33′51″/69°14′32″	Sericitic hydrothermal breccia	Jarositic leached breccia	5.97	1.8176	5.23	21.0 ± 1.3
COD-93-9	Sierra Gorda (Catalina)	Surface, Los Caballos open pit	22°51′54″/69°20′27″	Sericitic intrusive rock	Jarositic leached capping	5.32	1.0853	19.7	14.1 ± 0.6
COD-92-5	Telégrato	Surface	22°59′16″/69°04′35″	Quartz-tourmaline altered andesitic volcanics	Jarositic leached capping	2.557	0.7383	10.4	20.0 ± 1.0
COD-93-8	Lomas Bayas	Surface, 400 m south of La Tirana open cut	23°26′00″/69°31′00″	Granodiorite in fault zone	Adjoining vein gossan	8.84	2.6605	43.6	20.8 ± 0.8
CAKAR 15 (Alpers, 1986; Alpers and Brimhall, 1988)	Escondida			Sericitic porphyry (?)	Hematitic leached capping	7.69	1.9688	34.0	17.7 ± 0.7
CAKAR 16 (Alpers, 1986; Alpers and Brimhall, 1988)	Escondida			Sericitic porphyry (?)	Hematitic leached capping	6.03	1.2853	18.6	14.7 ± 0.6
CAKAR 17 (Alpers, 1986; Alpers and Brimhall, 1988)	Escondida			Sericitic porphyry (?)	Hematitic leached capping	8.65	2.0550	20.3	16.4 ± 0.7
CAKAR 19 (Alpers, 1986; Alpers and Brimhall, 1988)	Escondida			Sericitic porphyry (?)	Enrichment blanket (?)	9.02	2.0908	24.3	18.0 ± 0.7
COD-92-6	Angelina	Surface	24°23′54″/69°36′27″	Sericitic porphyry	Hematitic leached capping	9.07	4.0528	33.0	31.0 ± 1.0
COD-93-4	El Salvador	DDH S-1096, 60 m	26°15′34″/69°33′50″	Silicified andesitic volcanics	Jarositic leached capping, 5 m above sulfides	4.87	1.6312	20.7	23.1 ± 0.7
COD-93-2	La Coipa (Can Can)	Level 4,120 m	26°47′26″/69°16′10″	Argillized dacitic tuffs on edge of orebody	Jarositic leached capping	7.70	1.6174	55.3	14.5 ± 0.4
COD-93-11	Inca de Oro (Cerro La Campana)	Surface	26°45′58″/60°52′17″	Propylitic andesitic volcanics	Jarositic leached capping	2.99	0.6116	20.4	14.2 ± 0.6

$\lambda_\epsilon = 0.581 \times 10^{-10}\ yr^{-1}$; $\lambda_\beta = 4.962 \times 10^{-10}\ yr^{-1}$; $^{40}K/K = 1.167 \times 10^{-4}$ mole/mole.

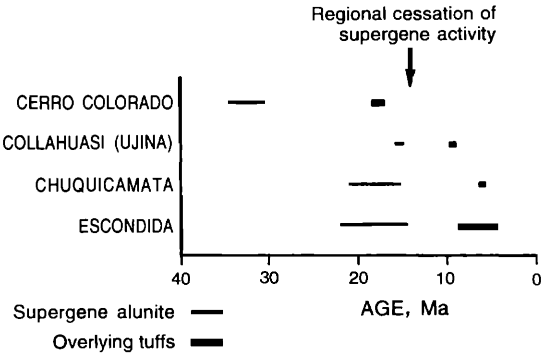

FIG. 6. Ages of alunites in supergene profiles and biotites in overlying ignimbrites and airfall tuffs from four porphyry copper deposits in northern Chile. Note the >5-m.y. time gaps between supergene alunite formation and tuff deposition, which suggests that argon loss from alunite as a result of heating during tuff emplacement did not take place. Supergene ages from Table 1; tuff ages from Vergara et al. (1986), Baker (1977), E. H. McKee and R. H. Sillitoe (unpub. data), and Alpers and Brimhall (1988).

unlikely to have formed at exactly the same time during an extended weathering event, there is no reason to ascribe the spreads of ages observed at Chuquicamata, MM, and Cerro Colorado to the effects of diffusive argon loss.

Argon loss induced by subsequent magmatism is not considered to be a problem because intrusive activity did not take place in any of the three porphyry copper belts after the supergene profiles were developed (e.g., Maksaev and Zentilli, 1988; Mpodozis and Ramos, 1990). The only magmatic products deposited after supergene activity had ceased are felsic volcanic units derived from distant caldera sources to the east. These comprise welded and nonwelded ignimbrites over the Cerro Colorado and Ujina deposits and thin airfall tuffs in the Radomiro Tomic-Chuquicamata-MM and Escondida districts. K/Ar dating of magmatic biotite separates shows that these volcanic products are at least 5 m.y. younger than the underlying or nearby supergene alunites (Fig. 6): 18.6 ± 0.3 to 17.3 ± 0.6 Ma (Vergara et al., 1986) compared to 34.3 ± 1.1 and 30.3 ± 1.1 Ma at Cerro Colorado; 9.3 ± 0.2 Ma (Baker, 1977) compared to 15.2 ± 0.5 Ma at Ujina; 8.6 ± 0.4 Ma (J.P. Hunt, 1970 *in* Mortimer et al., 1977; recalculated using the constants of Steiger and Jäger, 1977) or 6.1 ± 0.4 Ma (E.H. McKee and R.H. Sillitoe, unpub. data) compared to 19.0 ± 0.7 to 15.2 ± 0.5 Ma at Chuquicamata; and 8.7 ± 0.4 to 4.2 ± 0.2 Ma (Alpers and Brimhall, 1988) compared to 18.0 ± 0.7 to 14.7 ± 0.6 Ma at Escondida (Alpers and Brimhall, 1988). The thickest of these volcanic accumulations, ~50 m in several individual ignimbrite flows (Vergara et al., 1986), is present at Cerro Colorado and may be considered as the one most likely to have induced argon loss from the underlying alunite. However, argon loss seems highly unlikely because Cerro Colorado yielded the oldest supergene alunite ages in the study area and the largest gap (>10.3–<18.7 m.y.) between supergene alunite formation and postmineral felsic volcanism (Fig. 6). Moreover, one of the Cerro Colorado samples (COD-93-15; Table 1) was not covered by any of the ignimbrite flows, whereas the other was collected from the top of the sulfide enrichment zone about 50 m beneath their base.

Analytical procedures

The K/Ar dating was carried out in the laboratories of the U.S. Geological Survey at Menlo Park, California, using the standard isotope dilution procedures described by Dalrymple and Lanphere (1969). The age determinations were performed on powdered chips of alunite selected from veinlet interiors without the need for mineral separation.

Potassium analyses were carried out using lithium metaborate flux fusion-flame photometry techniques, the lithium acting as an internal standard (Ingamells, 1970). Argon analyses were performed using a five-collector system for simultaneous measurement of argon isotope ratios in a mass spectrometer operated in the static mode (Stacey et al., 1981). The precision of the data, shown as the ± value, is the estimated analytical uncertainty at one standard deviation. It represents uncertainty in the measurement of ^{40}Ar and K in the sample and is based on experience with replicated analyses in the Menlo Park laboratories. The decay constants used for ^{40}Ar are those adopted by the International Union of Geological Sciences Subcommission on Geochronology (Steiger and Jäger, 1977).

Incorporation of excess atmospheric ^{40}Ar into alunites is of no concern because mineral deposition was from supergene solutions which, as noted by Vasconcelos et al. (1994), should reflect the argon composition of the atmosphere.

Results and Discussion

Duration of supergene activity

On the basis of our alunite ages for seven porphyry copper deposits, five porphyry copper prospects, and one gold-silver deposit (Table 1; Figs. 1 and 7), oxidation and enrichment processes in northern Chile were active between about 34 and 14 Ma (early Oligocene to middle Miocene; Berggren et al., 1985). Four ages, 18.0 ± 0.7, 17.7 ± 0.7, 16.4 ± 0.7, and 14.7 ± 0.6 Ma, for supergene alunites from the Escondida porphyry copper deposit (Alpers, 1986; Alpers and Brimhall, 1988) also fall into this time interval. The supergene processes were active, at least intermittently, for a minimum of 2.6 to 5.0 m.y. at Chuquicamata (based on seven ages), 2.0 to 4.6 m.y. at Escondida (four ages), 1.8 to 6.2 m.y. at Cerro Colorado (two ages), and 0.4 to 1.6 m.y. at MM (two ages) if the ages are considered to be absolute and the analytical uncertainties quoted in Table 1 are taken into account.

K/Ar ages of 36.1 ± 0.6 and 36.0 ± 2.5 Ma reported by Gustafson and Hunt (1975) for supergene alunites from El Salvador fall just outside this interval and are in marked discaccord with our age of 23.1 ± 0.7 Ma for supergene alunite from El Salvador (Table 1) and with all other supergene alunite ages from the late Eocene to early Oligocene porphyry copper belt (see below). These two old ages, which were questioned by Clark et al. (1990) on geomorphologic grounds, are excluded from this discussion because they are only 3 m.y. younger or less than undoubted hypogene alunite from El Salvador (Gustafson and Hunt, 1975) and because none of the other localities has shown either such disparate supergene alunite ages or such a small time gap between hypogene and supergene activity. The origin of these two old "supergene" alunites remains enigmatic; however, they may be end-stage

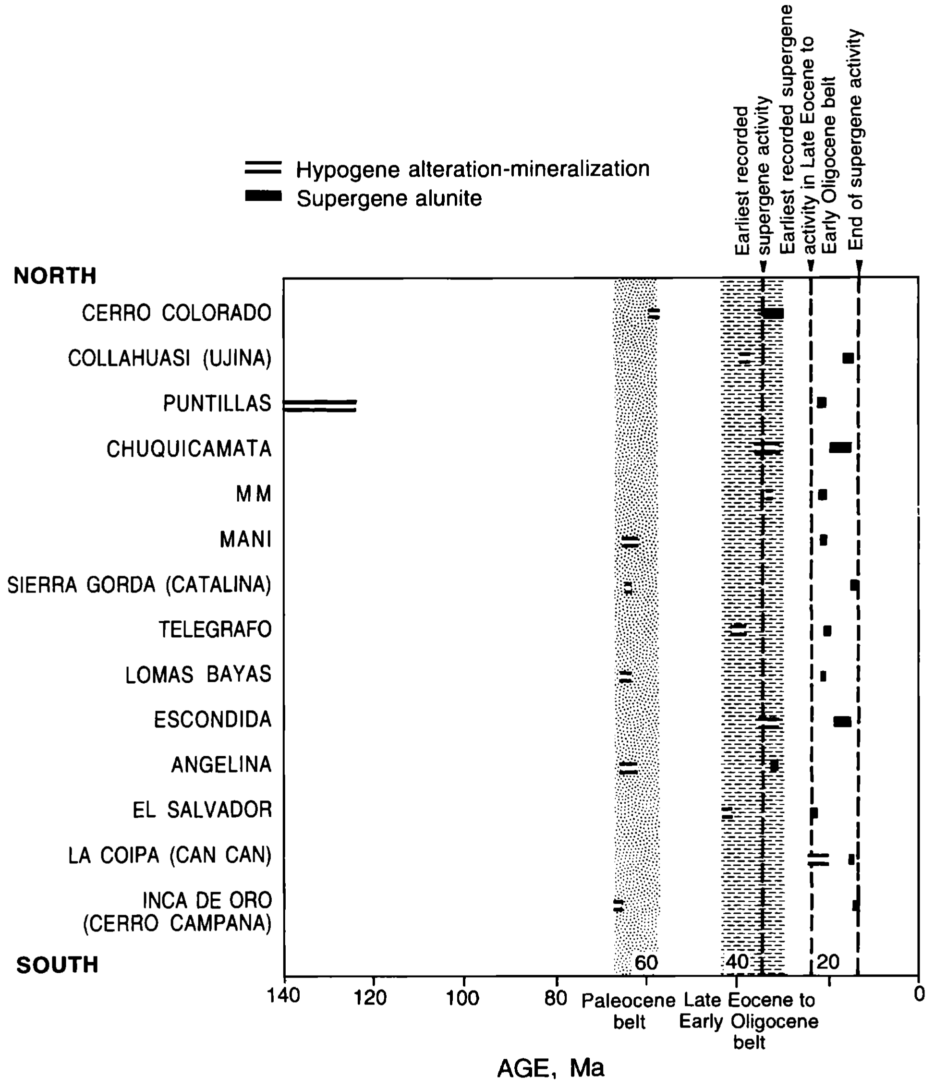

FIG. 7. North-south plot of hypogene and supergene (alunite) ages for porphyry copper deposits and prospects in northern Chile. Ages taken from Table 1 and Figure 1. Hypogene ages for the Maní and Angelina prospects are inferred on the basis of geographic position and ages of nearest deposits. The age ranges of the Paleocene and late Eocene to early Oligocene porphyry copper belts are approximated, along with the earliest recorded supergene activity in the Paleocene belt, the earliest recorded supergene activity in the late Eocene to early Oligocene belt, and the last recorded supergene activity in both belts.

hypogene products, supergene products contaminated heavily with hypogene alunite or sericite from their immediate host rocks, or, as proposed by Gustafson and Hunt (1975) but considered less likely by us, supergene products formed immediately after the cessation of hypogene activity.

The results of this radiometric dating program demonstrate clearly that alunite generation and, as a direct corollary, essentially all supergene activity in northern Chile, ceased in the middle Miocene at ~14 Ma (Fig. 7). This conclusion agrees well with the middle Miocene minimum age for supergene activity imposed by the region's landform chronology (Sillitoe et al., 1968; Mortimer, 1973; Mortimer et al., 1977) and very closely indeed with the 14.7 ± 0.6 Ma age for the cessation of supergene activity based on dating of alunites from the Escondida deposit (Alpers, 1986; Alpers and Brimhall, 1988).

The results show, however, that supergene oxidation and enrichment in northern Chile were active for a longer, although not necessarily continuous, period than appreciated previously: at least 20 m.y. (Fig. 7). Furthermore, the oldest alunite date available for each deposit must be a minimum age for the commencement of its supergene history because, at Cerro Colorado, Ujina, Chuquicamata, Escondida, Angelina, and El Salvador, hematitic leached capping, developed from preexisting sulfides enriched by supergene chalcocite (cf. Anderson, 1982), is present in the uppermost preserved parts of the supergene profiles. Moreover, at Chuquicamata, a zone of chalcocite enrichment is believed to have oxidized largely in situ to produce the antlerite-rich oxidized ore (Lindgren, 1917; Jarrell, 1944). At Escondida, Brimhall et al. (1985) calculated that at least 200 m of leached profile must have been eroded in order to account for all the copper contained in the present sulfide enrichment blanket. In the case of Cerro Colorado and Angelina, in the Paleocene belt, this conclusion implies that supergene activity took place before 34.3 ± 1.1 and 31.0 ± 1.0 Ma, respectively (Fig. 7). It is unlikely, however, that copper enrichment affected the late Eocene to early Oligocene deposits at that time, during the early Oligocene, because insufficient time is likely to have elapsed to unroof the copper-bearing parts of the systems; at least 2 km would need to be removed (e.g., Gustafson and Hunt, 1975). At none of the porphyry copper deposits studied does <~11 m.y. separate the time of deposit formation and the oldest supergene alunite age (Fig. 7). However, at La Coipa, where epithermal gold-silver deposition took place at depths of as little as 100 to 200 m beneath a partly preserved paleowater table (Sillitoe, 1991), supergene alunite formation (14.5 ± 0.4 Ma; Table 1) took place only about 6 m.y. after the conclusion of hypogene alteration (including alunite) and mineralization at about 23 to 20 Ma (Sillitoe, 1991; Fig. 7).

Supergene age correlations

All the deposits studied in the late Eocene to early Oligocene belt provide supergene alunite ages falling into a restricted interval of only ~9 m.y. (23.1 ± 0.7–14.7 ± 0.5 Ma; Table 1; Fig. 7). These alunites were formed ~23 to 11 m.y. after formation of the respective hypogene mineralization (Fig. 7). In contrast, a much broader range of ages (34.3 ± 1.1–14.1 ± 0.6 Ma; Table 1; Fig. 7) characterizes the Paleocene belt, where supergene processes were operative, at least at times, for a minimum of ~20 m.y. The alunite ages from the Paleocene belt may be interpreted in terms of unroofing of copper-bearing parts of the systems at different times: in the late Eocene or earliest Oligocene at Cerro Colorado and Angelina, but possibly 10 m.y. or more later at the other deposits and prospects (Fig. 7). Notwithstanding these older supergene alunite dates from Cerro Colorado and Angelina, our results, combined with those of Alpers (1986) for Escondida, suggest that supergene activity, or at least its advanced stages, in the Early Cretaceous, Paleocene, and late Eocene to early Oligocene porphyry copper belts and in the oldest, western part of the Maricunga gold-silver belt was broadly contemporaneous rather than taking place at different times. No evidence exists to support a temporally discrete enrichment event in each metallogenic belt. At Puntillas, in the Early Cretaceous belt (Fig. 7), any supergene profile developed before the early Miocene has been lost to erosion.

On the basis of these results, oxidation and copper enrichment may have been active at Cerro Colorado, Angelina, and probably elsewhere in the Paleocene belt while the late Eocene to early Oligocene porphyry copper deposits were being generated farther east (Fig. 8). The initial mineralization stage in the Maricunga gold-silver belt, between 25 and 20 Ma (Sillitoe et al., 1991), overlapped with oxidation and enrichment in the late Eocene to early Oligocene belt to the west, whereas the second stage of deposit generation in the eastern part of the Maricunga belt, from 14 to 12.5 Ma (Sillitoe et al., 1991), immediately postdated all appreciable supergene activity in northern Chile (Fig. 8). Moreover, the 14.5 ± 0.4 Ma age for supergene alunite from the La Coipa district confirms that deep oxidation (apparently without appreciable accompanying sulfide enrichment) of the gold-silver ore (Oviedo et al., 1991; Cecioni and Dick, 1992) took place near the end of the >20 m.y. of supergene activity in northern Chile (Fig. 8; cf. Sillitoe, 1991). Therefore, as summarized in Figure 8, supergene oxidation, with or without concomitant sulfide enrichment, was broadly contemporaneous with, albeit spatially separate from, hypogene ore formation during the Oligocene through middle Miocene interval in northern Chile.

The size and grade of porphyry copper systems in northern Chile are not factors that directly influence supergene chronologies because giant deposits, such as Chuquicamata and Escondida, underwent supergene alunite formation at broadly the same time as apparently minor prospects (Figs. 1 and 7). By the same token, supergene activity leading to the formation of major cumulative enrichment blankets was broadly coeval with that resulting elsewhere only in sulfide oxidation and leaching.

There is no discernable control exerted on supergene chronology by the morphotectonic settings of deposits. Most of the deposits and prospects dated are distributed throughout the Precordillera province, although Puntillas is located on the eastern boundary of the Coastal Cordillera (Fig. 3). The dated (21.1 ± 0.6 Ma) supergene activity at Puntillas took place after formation of the present morphotectonic provinces of northern Chile at the end of the Oligocene (Mortimer et al., 1974; Mortimer and Saric, 1975; Naranjo and Paskoff, 1985). However, oxidation and enrichment, at least at Cerro Colorado and Angelina, were active before this late Oligocene block-faulting event, during and possibly before the Oligocene pedimentation event that affected the entire region eastward from the Pacific littoral (Galli-Olivier,1967; Mortimer and Saric, 1975). In contrast, the recorded supergene oxidation ± enrichment at all other deposits studied took place between the Oligocene and middle Miocene (Atacama) pedimentation events.

The latitudinal position of the deposits and prospects does not appear to correlate with the timing of the supergene activity, as shown by the occurrence of 14 to 15 Ma alunite ages both in the north (Ujina) and south (Cerro La Campana, La Coipa) of the 7° transect studied (Figs. 1 and 7). Nor does present elevation seem to have any bearing on the age of supergene activity given that ≈14 Ma alunites were dated from both Cerro La Campana and, farther east and 2,300 m higher, at La Coipa (Fig. 1).

Alunite samples collected at the present surface, which is essentially the middle Miocene pediplain over much of the region, range in age from 34.3 ± 1.1 to 14.1 ± 0.6 Ma. This range is little different from that of 30.3 ± 1.1 to 14.5 ± 0.4 Ma for the ages of alunites from subsurface sites. However, insufficient data are available to assess possible vertical age progressions within individual supergene profiles. Nevertheless, at Cerro Colorado, the older alunite (34.3 ± 1.1 Ma; Table 1) is from the highest and therefore oldest preserved part of the leached capping, whereas the younger alunite (30.3 ± 1.1 Ma; Table 1) was collected from the top of the underlying enrichment blanket, probably the site of most recent supergene activity. The principal post-middle Miocene

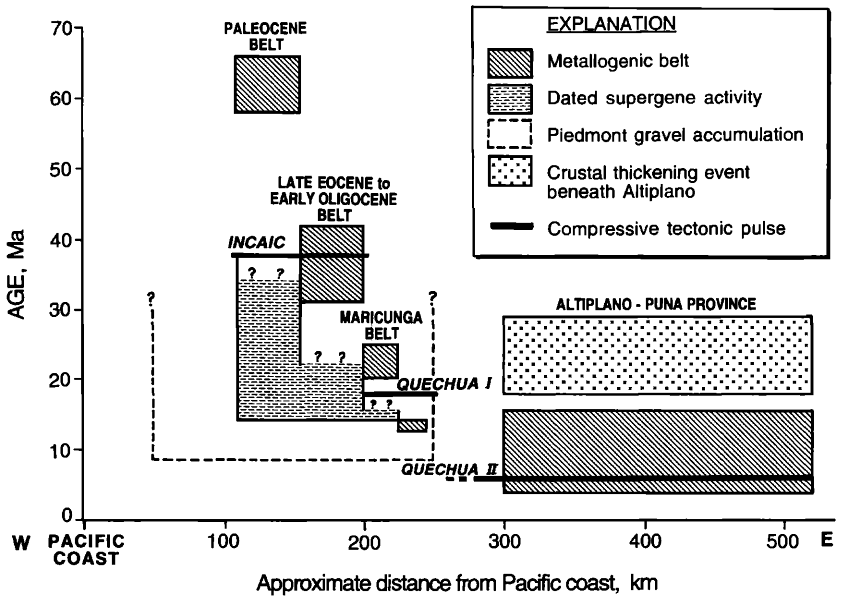

FIG. 8. Ages of hypogene porphyry copper-molybdenum–gold systems (Fig. 1), supergene oxidation and enrichment (Fig. 1), piedmont gravel accumulation (e.g., Naranjo and Paskoff, 1985), and compressive tectonism (McKee and Noble, 1990; Sampere et al., 1990) during the Tertiary in northern Chile and contiguous western Bolivia. Widths of metallogenic belts and their distances from the Pacific coast are approximated.

modification of the landscape in northern Chile, the incision of the transverse valleys, resulted in partial or complete destruction of any preexisting supergene profiles (Sillitoe et al., 1968; Mortimer, 1973). This effect is observed at the Cerro Colorado deposit, where the early Oligocene supergene profile is exposed on the southern wall of a late Miocene and Pliocene canyon.

Application to Exploration

Timing of supergene activity vs. piedmont gravel accumulation

At least the second half, and probably more, of the >34 to 14 Ma interval of supergene oxidation and enrichment in northern Chile, at least north of approximately 22° S, coincided temporally with accumulation of the piedmont gravel sequences and their intercalated ignimbrite flows (Fig. 8). These materials constitute the Altos de Pica Formation (Galli and Dingman, 1962; Naranjo and Paskoff, 1985), Calama Formation (Naranjo and Paskoff, 1981), and correlative units. The ignimbrites are dated at ~24 to 9 Ma (Mortimer et al., 1974; Baker, 1977; Naranjo and Paskoff, 1985; Vergara et al., 1986), but gravels beneath the oldest dated ignimbrites clearly are older still (e.g., Mortimer et al., 1974; Naranjo and Paskoff, 1985). In fact, an ignimbrite flow in the lower middle part of an even older, deformed gravel sequence, assigned to the Sichal Formation, was dated at 34.1 ± 1.0 Ma (Maksaev, 1978). Therefore porphyry copper deposits concealed beneath appreciable thicknesses of gravels and/or ignimbrites north of approximately latitude 22° S are less likely to have developed mature supergene profiles than those that avoided burial. This is because once an appreciable thickness, say 50 m, of gravels and ignimbrites had accumulated, paleowater tables are likely to have been located within the gravels rather than in the subjacent mineralized bedrock, a situation that precludes oxidative weathering of sulfides and release of the copper required for enrichment.

Nevertheless, major oxidized and enriched zones may be present where concealment by gravels and/or ignimbrites commenced relatively late in, or after completion of, the supergene event, as at Ujina in the Collahuasi district where the capping ignimbrite is dated at 9.3 ± 0.2 Ma (Baker, 1977). This situation is thought to be more widespread south of approximately latitude 22° S because the gravel-ignimbrite sequences, including the Atacama gravels (Mortimer, 1973; Naranjo and Paskoff, 1980), accumulated mainly between 17 and 10 Ma (Clark et al., 1967; Sillitoe et al., 1968; Naranjo and Paskoff, 1980; C. Mpodozis, written commun., 1995). Appreciable oxidation and enrichment also would have been possible in the early Oligocene, prior to gravel and ignimbrite accumulation, as seems to have been the case at Cerro Colorado. Indeed, the apparent cessation of oxidation and enrichment soon after ~30 Ma at Cerro Colorado could be ascribed to initial burial of the deposit beneath piedmont gravels of the Altos de Pica Formation.

Therefore, it may be concluded that search for major cumulative enrichment blankets beneath the thick piedmont gravel sequences widespread in the Paleocene and late Eocene to early Oligocene porphyry copper belts of northern Chile is a risky endeavor, at least north of approximately 22° S. The shallowly covered areas, which potentially may be defined using geophysical techniques, are the most likely to constitute attractive exploration targets. Radiometric dating of biotites from ignimbrite or airfall tuff interbeds in the gravel sequences would help to define the supergene potential of any mineralized bedrock beneath them.

The Oligocene to middle Miocene piedmont gravel sequences in northern Chile are host to several major exotic copper deposits, in which chrysocolla, atacamite, and/or copper wad are the principal ore minerals (e.g., Fam, 1979; Sillitoe, 1990). Most of these deposits span the unconformable contact between bedrock and the overlying gravels (Fig. 2), although stratigraphically higher gravel sequences also may be mineralized. Copper in these exotic deposits was derived by lateral solution transport from actively forming supergene profiles, especially those undergoing enrichment. Major examples are Mina Sur up to 6 km from Chuquicamata (Mortimer et al., 1977) and Damiana up to 4 km from El Salvador (Rojas and Müller, 1994). The existence of exotic copper deposits adjacent to some oxidized and enriched porphyry copper deposits in northern Chile underscores further the temporal overlap between supergene activity and piedmont gravel accumulation. It also raises the possibility that gravel sequences appearing barren at surface may host exotic copper mineralization at depth, especially in the vicinity of the bedrock contact.

Timing of supergene activity vs. hypogene mineralization

It was noted above that essentially all supergene activity in northern Chile had ended by the time the eastern part of the Maricunga gold-silver belt was formed (Fig. 8). Similarly, all porphyry copper systems farther east, in northwestern Argentina and western Bolivia, were emplaced between ≈15 and 4 Ma (Sillitoe, 1977, 1988; Losada-Calderón et al., 1994) and so are unlikely to have been affected by cumulative supergene enichment. However, a few older porphyry copper prospects, of Carboniferous to Permian age in northwestern Argentina and contiguous Chile (Sillitoe, 1977) and Triassic age in northern Chile (J.C. Marquardt, pers. commun., 1994), potentially could have undergone enrichment although none has been documented.

In the Andean Cordillera of central Chile (~35° S), substantial but nevertheless relatively immature, early cycle sulfide enrichment has taken place at the El Teniente (Lindgren and Bastin, 1922; Howell and Molloy, 1960) and Río Blanco-Los Bronces (Warnaars et al., 1985) porphyry copper deposits since their emplacement only 4 to 5 m.y. ago (see Sillitoe, 1988), presumably because annual precipitation was probably five to ten times greater (El Teniente, 1912–53, 1,051 mm/yr; Fuenzalida, 1966) than that in northern Chile and contiguous parts of northwestern Argentina and western Bolivia during the same period. In fact, it is suspected that supergene oxidation and enrichment are active currently at El Teniente and Río Blanco-Los Bronces in view of the large volumes of copper-bearing ground water that exit both deposits. This part of central Chile possesses climatic and uplift (cf. Skewes and Holmgren, 1993) regimes that may be similar to those that existed in northern Chile during active Oligocene through middle Miocene oxidation and enrichment.

Exploration for major cumulative enrichment blankets should therefore be restricted to the late Eocene to early Oligocene, Paleocene, and older porphyry copper belts in northern Chile, where post-14 Ma erosion has been insufficient to cause appreciable destruction of most Oligocene to middle Miocene supergene profiles.

Regional and Global Controls on Supergene Processes

Regional controls

Anderson (1982), Brimhall et al. (1985), and Sillitoe (1990) all emphasized that efficient cumulative enrichment, as in northern Chile, is favored by tectonically induced uplift. Continuous or episodic uplift causes depression of water tables, thereby exposing, either abruptly or gradually, more sulfides to the effects of oxidative weathering.

Regionally extensive but brief pulses of compressive tectonism, defined in Peru, are believed to have affected much of the central Andes, including northern Chile, in the middle Eocene (~43 Ma; Incaic II phase), early Miocene (~18 Ma; Quechua I phase), and late Miocene (~6 Ma; Quechua II phase) (McKee and Noble, 1990; Fig. 8). The Incaic phase is recognized in northern Chile (Maksaev and Zentilli, 1988), where recent studies have shown it to have been a deformation event linked to the sinistral transpression that generated the Domeyko fault system along the late Eocene to early Oligocene belt between about 42 and 38 Ma (Tomlinson et al., 1994; Yáñez et al., 1994). High-angle reverse faulting and the initiation of crustal thickening, defined using the petrochemical evolution of magmatic products, commenced between 18 and 14 Ma in the Maricunga belt at latitudes 26° to 28° S (Kay et al., 1994) and may correspond to the Quechua I phase. The Quechua II phase, however, is not defined clearly in northern Chile, although it may be represented farther east. If the uplift essential for efficient oxidation and enrichment is linked closely in time to one or more brief tectonic pulses, then the Incaic phase could have instigated or accelerated supergene activity in the Paleocene and older porphyry copper belts (Fig. 8). However, none of these tectonic pulses could have triggered oxidation and enrichment of the late Eocene to early Oligocene deposits unless the uplift was substantially longer lived than the causative tectonism.

Integrated geologic studies of the Bolivian Altiplano region (latitudes 18°–22° S), east of the Andean Cordillera (Fig. 3), suggest that compressive deformation there was particularly active over a maximum interval of 29 to 18 Ma (Sampere et al., 1990). This conclusion agrees well with an age of ~30 Ma for the initiation of crustal thickening beneath the Altiplano, as deduced from isotopic studies (Miller and Harris, 1989). If this tectonic event had regionally extensive repercussions farther west, it may have provided the uplift essential for effective supergene oxidation and enrichment in part of northern Chile. Certainly the central Andean chain must have attained an appreciable elevation by 14 Ma in order to contribute to the rain-shadow effect invoked to explain the climatic dessication initiated at that time (Alpers and Brimhall, 1988). Farther south, however, in the Puna of northwestern Argentina (latitudes 24°–26° S) and the Maricunga belt, crustal thickening and plateau uplift do not appear to have begun until about 18 to 15 Ma (Kay et al., 1994; Vandervoort et al., 1995). This apparently later initiation of Andean uplift may be correlated with the delayed appearance of piedmont gravel aggradation noted previously and, potentially, could imply a later commencement of oxidation and cumulative enrichment. In summary, correlations between uplift chro-

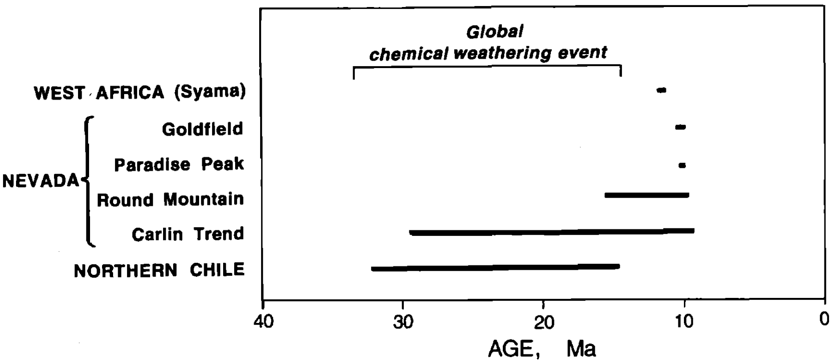

FIG. 9. Ages of supergene alunites from copper and gold deposits in northern Chile (this study; Alpers and Brimhall, 1988), gold deposits in Nevada (Ashley and Silberman, 1976; Berger, 1985; Tingley and Sander, 1988; Sillitoe and Bonham, 1990; Arehart et al., 1992; Sillitoe and Lorson, 1994; Vasconcelos et al., 1994), and supergene jarosite from West Africa (Vasconcelos et al., 1994) compared with a period of globally extensive chemical weathering proposed by Rea (1993).

nology and supergene activity in northern Chile remain poorly understood, but it is suspected that uplift tended to be a protracted rather than a short-lived, pulsed process.

The onset of hyperaridity and the consequent cessation of appreciable supergene activity in northern Chile were related by Alpers and Brimhall (1988) to the interplay between the tectonic emergence of the central Andean mountain chain as a physical barrier and the cooling of the ancestral Humboldt current as the Antarctic ice cap became established at approximately 15 to 13 Ma. However, more recent studies have shown that Antarctic glaciation began >20 m.y. earlier in the late Eocene to early Oligocene (Barron et al., 1991; Zachos et al., 1992). Consequently, Andean uplift may have been the fundamental factor controlling middle Miocene desertification in northern Chile, in the same way that kilometer-scale uplift in western North America and the Himalaya-Tibet has been a major cause of climatic cooling and desertification in parts of the northern hemisphere (Ruddiman and Kutzbach, 1989).

Possible global controls

The documented >34 to 14 Ma interval for supergene oxidation and enrichment of porphyry copper deposits in northern Chile encompasses all available supergene alunite ages from deeply oxidized gold deposits in Nevada, i.e., from about 30 to 9 Ma (Ashley and Silberman, 1976; Tingley and Berger, 1985; Sander, 1988; Bloomstein et al., 1990; Sillitoe and Bonham, 1990; Arehart et al., 1992; Arehart and O'Neil, 1993; Sillitoe and Lorson, 1994; Vasconcelos et al., 1994; Fig. 9), as well as with the most likely timing of the principal supergene enrichment of porphyry copper deposits in southern Peru (Clark et al., 1990) and southwestern North America (Livingston et al., 1968). This interval, in particular that defined for northern Chile, corresponds with a globally extensive period of chemical weathering, from the Eocene-Oligocene boundary (36.6 Ma; Berggren et al., 1985) to the middle Miocene (Rea, 1993; Fig. 9). This 20-m.y. interval is considered by Rea (1993) to have been characterized by relatively low-lying continents subjected to low rates of mechanical weathering, as corroborated by records from the oceans (e.g., Hovan and Rea, 1992). Furthermore, the middle Miocene cessation of deep chemical weathering documented at several localities in North America and West Africa (Fig. 9), as well as that well defined in northern Chile, is suggested by Vasconcelos et al. (1994) to be attributable to global rather than simply local climatic dessication.

Nevertheless, although supergene alunite formation seems to have been most widespread during the middle Tertiary interval of deep weathering, alunite continued to form under suitable conditions until the present day. For example, in the central Andes, supergene alunite formed in a thin, immature oxidation zone at high elevations (>4,000 m) in the Nevados del Famatina porphyry copper system, Argentina (R.H. Sillitoe, unpub. data), where it must be appreciably younger than the 4 Ma age for hypogene alteration and mineralization (Losada-Calderón et al., 1994).

Acknowledgments

Logistic support and/or permission to collect alunite samples for this study were generously provided during 1991 to 1993 by Chevron Minera Corporation of Chile, Cía. Minera Cerro Colorado Ltda., Cía. Minera Doña Ines de Collahuasi, CODELCO-Chile, CRA Exploration Pty Ltd., Empresa Minera de Mantos Blancos S.A., Minera Outokumpu Chile S.A., Shell Chile, and Sociedad Minera Pudahuel. Sampling assistance and geologic information were given freely by many geologists, in particular, Alejandro Cecioni, Francisco Eggers, Carlos Llaumett, Juan Carlos Marquardt, Marcial Maturana, Guillermo Müller, Juan Carlos Toro, and Tomas Vila. K/Ar dating was carried out in the laboratories of the U.S. Geological Survey at Menlo Park, California, as part of a project on geochronology of igneous rocks and ore deposits in volcanic terranes.

Valuable comments on the manuscript were contributed by Francisco Camus, David John, Constantino Mpodozis, José Antonio Naranjo, James Rytuba, Nicolás Saric, and two *Economic Geology* reviewers. This is a contribution to IGCP Project 342, "Age and isotopes of South American ores."

June 1, September 6, 1995

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