Rubidium as a Guide to Ore in Chilean Porphyry Copper Deposits

G. A. ARMBRUST, J. OYARZÚN, AND J. ARIAS

Abstract

Hypogene mineralization in porphyry copper deposits is characteristically associated with zones of potassic alteration. The mineralization and hydrothermal alteration are thought to be produced by an aqueous phase which has separated from a crystallizing magma. Due to the similarity in geochemical characteristics of K and Rb, Rb can be incorporated in K minerals that crystallize from a magma. The Rb ion is only 0.14Å larger than the K ion, but this size difference results in a higher bonding energy between K and O than between Rb and O. Therefore, when K minerals crystallize from a magma, K is preferentially removed with respect to Rb. The Rb tends to concentrate in the residual melt. If an aqueous phase separates from a magma during late stages of crystallization, it should have relatively higher Rb concentrations and low K/Rb ratios. High Rb concentrations and low K/Rb ratios might therefore be expected in rocks that have undergone potassic alteration.

Wide zones of potassic alteration are closely associated with the orebodies at the Chilean porphyry copper deposits in the El Teniente (Braden), Rio Blanco, and Los Broncos (Disputada) mines. Therefore, the distribution of Rb and its relationship to ore and alteration at the three deposits is determined. As K replaces Ca in plagioclase, and Sr is geochemically related to Ca, the distribution of Sr is also determined. Background values for Rb and Sr are difficult to determine, as all accessible parts of the intrusions near the deposits are hydrothermally altered. Background values for intrusive rocks were obtained from 17 samples of unaltered intrusive bodies not associated with porphyry copper deposits.

The following conclusions, though based on the study at El Teniente, Rio Blanco, and Los Broncos, may also be applicable to other porphyry copper deposits.

1. Rocks that have undergone potassic or sericitic alteration have a two- to threefold increase in Rb and low K/Rb ratios. As these types of alteration characteristically accompany mineralization in porphyry copper deposits, Rb distribution may be useful to locate favorable alteration zones for porphyry copper exploration. The highest anomalies are found in mafic host rocks, which have low Rb background values, though anomalies can also be detected in rocks as siliceous as quartz monzonite.

2. A twofold increase in Rb in the propylitic zone at El Teniente produces an anomaly which extends more than 400 meters beyond the margin of the orebody. No corresponding increase in K was observed. The Rb anomaly represents an enlarged target enclosing the zones of alteration commonly associated with porphyry copper mineralization.

3. Weathering does not affect the distribution of Rb in rocks from the leached capping at El Teniente. Due to this immobility of Rb, weathering of the potassic zone in porphyry copper deposits should not destroy the Rb anomaly. The distribution of Rb could be a useful tool to locate potassic alteration zones in areas of tropical weathering, for example, in the southwest Pacific and in Central America.

4. Addition of Rb and removal of Sr during hypogene alteration can produce high Rb/Sr anomalies which extend out through all of the zones of hydrothermal alteration. However, care must be taken in interpreting the significance of Rb/Sr anomalies because they may simply indicate extensive removal of Sr during normal weathering processes.

5. Contouring the Rb values may be useful for quantitatively mapping the extent of K metasomatism.

6. Anhydrite is readily dissolved and removed by acid meteoric waters. In deposits where anhydrite is an abundant hypogene alteration product, Sr depletion can be used as a quantitative guide to the degree of supergene activity.
Introduction

In the last few years, much has been written concerning the nature and origin of porphyry Cu-Mo deposits (Lowell and Guilbert, 1970; Rose, 1970; Mitchell and Garson, 1972; Sillitoe, 1973). Although no two deposits are exactly alike, a few geological characteristics are shared by nearly all of them. A striking feature is the well-developed zonal pattern of wall-rock alteration. Lowell and Guilbert (1970) state that the upward and outward sequence of alteration zones is potassic (dominant minerals are K-feldspar, biotite, sericite, quartz, anhydrite), phyllic (quartz, sericite, pyrite), argillic (quartz, kaolin, montmorillonite, sericite), and propylitic (chlorite, epidote, carbonates). Deposits need not contain all four zones, but those present occur in the above-mentioned order.

The chemical environment of hydrothermal alteration is clearly summarized by Meyer and Hemley (1967). The mineral assemblage in the potassic zone represents high temperature alteration where base exchange reactions involving replacement of Na and Ca by K predominate. The common inorganic acids in hydrothermal fluids do not ionize readily at high temperatures, so the K+/H+ ratio remains too high for significant hydrolysis to occur. K-feldspar rather than sericite is the stable K mineral under these conditions. K need not be added if the rocks are sufficiently rich in K. However, in intermediate to mafic rocks, potassic alteration may be accompanied by K metasomatism.

The main chemical reactions in the sericitic (phyllic) zone are due to strong hydrolytic activity, that is, H metasomatism. Hydrogen ion concentrations and activities are sufficiently high to displace Na and Ca from plagioclase. Sericite is the stable K mineral in this assemblage. The boundary between the potassic and phyllic alteration zones is typically sharp, and may be due to mixing of the hydrothermal fluids with cool meteoric water, or due to adiabatic expansion and cooling of the hydrothermal fluid as it passes into the upper fractured portion of the subvolcanic stock (Sheppard et al., 1971; Rose, 1970). Hydrolytic activity then usually decreases outward toward the propylitic zone.

Hypogene mineralization is typically associated with potassic alteration and the adjacent inner edge of the phyllic zone. As these alteration types commonly involve an increase in the K content, and Rb has geochemical characteristics that are very similar to those of K, Rb values should be expected to increase in the zone of potassic alteration (Armbrust et al., 1971). Thus, distribution of Rb in three Chilean deposits was determined to see if the Rb...
TABLE I. Ionic Radius (r), Electronegativity (e), and Ionization Potential (I) for K and Rb (from Taylor, 1965)

<table>
<thead>
<tr>
<th></th>
<th>r(Å)</th>
<th>e</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>1.33</td>
<td>0.80</td>
<td>4.34</td>
</tr>
<tr>
<td>Rb</td>
<td>1.47</td>
<td>0.80</td>
<td>4.18</td>
</tr>
</tbody>
</table>

holes in the breccia pipe at Los Bronces. Each sample weighed approximately 500 grams and consisted of one or two rock fragments. Samples containing as little vein material as possible were collected. Unaltered rock samples collected from outcrops located more than 3 km from the mines were used to determine background values.

All samples were described, then split; one-half was saved for thin section preparation; the rest was crushed in a steel mortar and ground in an agate mortar to minus 200 mesh for chemical analysis. K was determined by atomic absorption spectroscopy after total decomposition with a mixture of hydrofluoric-perchloric acids. Rb and Sr were determined by X-ray fluorescence on pressed powder pellets. USGS standard rocks AGV-1, GSP-1, BCR-1, and G2 were used to construct calibration curves. Precision of the K, Rb, and Sr determinations was ±4 percent, ±4 percent, and ±3 percent, respectively, at the 95 percent confidence level.

**Discussion**

K and Rb have similar ionic radii, electronegativities, and ionization potentials (Table 1); thus, Rb is preferentially incorporated in K minerals rather than forming its own minerals. The only significant difference between the two elements is a slightly larger size of the Rb ion (Rb, 1.47 Å; K, 1.33 Å), which causes bonding energy between K and O to be slightly higher than between Rb and O. Therefore, when K minerals crystallize from a magma, K is preferentially removed and Rb tends to concentrate in the residual melt.

K, Rb, and Sr abundances in andesites and associated rocks of the circum-Pacific belt (Table 2) show that both K and Rb increase with increasing content in the ore zone is sufficiently high to serve as an indicator of the degree of potassic alteration. Likewise, Sr also may vary systematically with potassic alteration. K replaces Ca in plagioclase, and Sr is geochemically related to Ca; thus Sr concentration in the altered rocks should decrease. An increase in Rb and corresponding decrease in Sr in the potassic zone should result in a substantial increase in the Rb/Sr ratio. All samples collected were therefore analyzed for both Rb and Sr.

**Sampling Methods and Analytical Techniques**

Rock samples were collected from the El Teniente (Braden), Rio Blanco, and Los Bronces (Disputada) deposits (Fig. 1). A total of 140 samples were collected at El Teniente on a 40-meter interval from mine workings on the T-5 level (Fig. 2), and from nine diamond drill holes which penetrated upward into the zone of supergene enrichment or outward into the zone of propylitic alteration. A total of 39 samples were collected from the mine workings on the T-9 level at Rio Blanco, and from two drill holes in the breccia pipe at Los Bronces. Each sample weighed approximately 500 grams and consisted of one or two rock fragments. Samples containing as little vein material as possible were collected. Unaltered rock samples collected from outcrops located more than 3 km from the mines were used to determine background values.

All samples were described, then split; one-half was saved for thin section preparation; the rest was crushed in a steel mortar and ground in an agate mortar to minus 200 mesh for chemical analysis. K was determined by atomic absorption spectroscopy after total decomposition with a mixture of hydrofluoric-perchloric acids. Rb and Sr were determined by X-ray fluorescence on pressed powder pellets. USGS standard rocks AGV-1, GSP-1, BCR-1, and G2 were used to construct calibration curves. Precision of the K, Rb, and Sr determinations was ±4 percent, ±4 percent, and ±3 percent, respectively, at the 95 percent confidence level.

K and Rb have similar ionic radii, electronegativities, and ionization potentials (Table 1); thus, Rb is preferentially incorporated in K minerals rather than forming its own minerals. The only significant difference between the two elements is a slightly larger size of the Rb ion (Rb, 1.47 Å; K, 1.33 Å), which causes bonding energy between K and O to be slightly higher than between Rb and O. Therefore, when K minerals crystallize from a magma, K is preferentially removed and Rb tends to concentrate in the residual melt.

K, Rb, and Sr abundances in andesites and associated rocks of the circum-Pacific belt (Table 2) show that both K and Rb increase with increasing

**Table 2. K, Rb, and Sr Concentrations in Rocks of the Circum-Pacific Belt**

<table>
<thead>
<tr>
<th></th>
<th>K</th>
<th>Rb</th>
<th>K/Rb</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Al basalt</td>
<td>0.33</td>
<td>9.6</td>
<td>344</td>
<td>328</td>
</tr>
<tr>
<td>Basaltic andesite</td>
<td>0.91</td>
<td>14</td>
<td>650</td>
<td>430</td>
</tr>
<tr>
<td>Andesite</td>
<td>1.33</td>
<td>31</td>
<td>430</td>
<td>385</td>
</tr>
<tr>
<td>Dacite</td>
<td>1.70</td>
<td>44</td>
<td>386</td>
<td>460</td>
</tr>
<tr>
<td>Rhyolite</td>
<td>2.81</td>
<td>108</td>
<td>250</td>
<td>125</td>
</tr>
</tbody>
</table>

Rubidium in Chilean Porphyry Copper Deposits

Table 3. Rb Abundance (ppm) in Various Volcanic Rocks

<table>
<thead>
<tr>
<th></th>
<th>Basalt</th>
<th>Andesite</th>
<th>Dacite</th>
<th>Rhyolite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Circum-oceanic1</td>
<td>20 (25)</td>
<td>36 (65)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Continental1</td>
<td>26 (106)</td>
<td>46 (4)</td>
<td>55 (4)</td>
<td>133 (105)</td>
</tr>
<tr>
<td>Farellones formation</td>
<td>43 (12)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

( ) = Number of samples

1 Rocks from Japan, New Zealand, and Puerto Rico.

2 Rocks from Antarctica, Tasmania, Karroo, New Zealand, and North America (data from Heier and Billings, 1970).

silica content, but Rb increases at a higher rate (Taylor, 1969). Assuming that the various rock types are produced by fractional crystallization, these data support the contention that Rb is preferentially concentrated in the residual melt. If an aqueous phase separates from a magma during the late stages of crystallization, the aqueous phase should have a high Rb concentration and a low K/Rb ratio relative to the magma that crystallized at an earlier stage. Therefore, high Rb concentrations and low K/Rb ratios relative to mafic or intermediate rocks should be expected in rocks that have undergone potassic alteration.

Determination of Rb background values for unaltered host rocks is essential for the evaluation of chemical data from hydrothermally altered equivalent rocks. Porphyry copper deposits are associated with stocks or dikelike intrusions of dioritic to granitic rock which have been emplaced into various types of host rocks at relatively shallow depths. These host rocks vary from metasediments, metavolcanics, and gneisses at Mineral Park, Arizona (Eidel et al., 1968), to limestones, sandstones, and shales at Ely, Nevada (Fournier, 1967), to andesites, rhyolites, and diorites at Toquepala, Peru (Richard and Courtright, 1958). However, the most common host rocks for the intruding magma are intermediate to mafic volcanics or hypabyssal intrusive rocks. This is particularly true for the South American deposits and is in agreement with the model proposed by Sillitoe (1973) which relates porphyry copper deposits to calc-alkaline volcanic complexes.

Background abundance of Rb in volcanic rocks of the circum-Pacific belt (Table 2) and in circum-oceanic and continental volcanics, including 12 samples of fresh andesites from the Lower Tertiary Farellones formation, host rocks for the El Teniente, Rio Blanco, and Los Bronces deposits of central Chile (Table 3), shows that Rb abundances for basalt-andesite are commonly less than 50 ppm. For rocks as siliceous as dacite, the Rb content should be less than 60 ppm. It is difficult to determine useful background values for rhyolites as their Rb contents are generally highly variable. Concentrations as high as 200 ppm are not uncommon.

About 70 percent of the mineralization in the typical porphyry copper deposit is found in the intrusive rocks (Lowell and Guilbert, 1970); the rest occurs in the surrounding, preore wall rocks. It is often impossible to collect unaltered samples of the intrusive rocks. Centers of mineralization and alteration coincide with the cupolas of the intrusive stocks, and the altered cupolas may be the only part of the intrusion that is exposed at the surface. Thus, unaltered samples of related intrusions are nearly impossible to collect. Hence, background Rb values must be obtained from unaltered intrusives which are not directly associated with porphyry copper deposits.

K, Rb, and Sr concentrations for intrusive rocks of the Similkameen batholith, British Columbia, the Coast Mountains batholith, British Columbia, and the Snowy Mountains area, NSW, Australia (Table 4) show that Rb increases with increasing K during differentiation (Pető, 1973; Culbert, 1972; and Kolbe and Taylor, 1966). Unlike the calc-alkaline volcanic sequence (Table 2), the intrusive rocks show only a slight decrease in the K/Rb ratio with increasing differentiation.

Background values for Rb, K, and Sr for intrusive rocks in Chile were determined on 43 samples from 17 unaltered intrusions of Paleozoic to Tertiary age. The modal composition of each sample is plotted in Figure 3, and concentrations of K, Rb, and Sr are tabulated in Table 5. The only apparent difference

Table 4. K, Rb, and Sr in Some Canadian and Australian Intrusive Rocks

<table>
<thead>
<tr>
<th></th>
<th>No. of samples</th>
<th>K%</th>
<th>Rb ppm</th>
<th>K/Rb</th>
<th>Sr ppm</th>
<th>Ref.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diorite</td>
<td>14</td>
<td>1.30</td>
<td>42</td>
<td>310</td>
<td>546</td>
<td>1, 2</td>
</tr>
<tr>
<td>Quartz diorite</td>
<td>28</td>
<td>1.34</td>
<td>39</td>
<td>341</td>
<td>714</td>
<td>1, 2</td>
</tr>
<tr>
<td>Granodiorite</td>
<td>53</td>
<td>2.10</td>
<td>79</td>
<td>284</td>
<td>650 (33)</td>
<td>1, 2, 3</td>
</tr>
<tr>
<td>Quartz monzonite</td>
<td>18</td>
<td>2.39</td>
<td>105</td>
<td>228</td>
<td>407</td>
<td>1, 2</td>
</tr>
<tr>
<td>Granite and pegmatite</td>
<td>10</td>
<td>3.79</td>
<td>150</td>
<td>253</td>
<td>86</td>
<td>1, 2</td>
</tr>
</tbody>
</table>

1 References: 1, Pető, 1973 (British Columbia).
2, Culbert, 1972 (British Columbia).
3, Kolbe and Taylor, 1966 (Australia).

( ) = Number of samples, if different from column two.
FIG. 3. Modal composition of 43 rock samples from 17 intrusive bodies in Chile. The ages of the intrusions range from Early Paleozoic to late Tertiary. Quartz, K-feldspar, and plagioclase contents were determined by point counting. The results were recalculated to 100 percent and plotted on this ternary diagram in order to assign rock names. The mean K, Rb, and Sr contents for these rocks are tabulated in Table 5.

between the results tabulated in Table 4 (rocks from British Columbia and New South Wales) and those in Table 5 (rocks from Chile) is the generally lower concentration of Sr in the Chilean intrusives. The high Rb values for the granites in Chile is probably not significant since this value is based on only two samples.

To determine the effects of low-grade metamorphism or deuteric alteration on the distribution of Rb in the intrusive rocks, the 43 samples were subdivided into three groups: fresh, slightly altered, and moderately altered. Both feldspars in the fresh samples contain little or no alteration, and ferromagnesian minerals are fresh. In slightly altered samples one feldspar, usually plagioclase, is cloudy, containing moderate amounts of sericite and other clay minerals. Biotite and hornblende are usually fresh, although in some samples they may be partially replaced by chlorite. In the moderately altered samples, both feldspars are cloudy, although K-feldspar may be distinguished from plagioclase. Ferromagnesian minerals are partially to completely replaced by chlorite.

No significant difference was noted in the abundance of Rb in the fresh, slightly altered, or moderately altered samples listed in Table 6. From these results, it is concluded that low-grade metamorphism or deuteric alteration does not appreciably affect the Rb content of the intrusive rocks.

The El Teniente (Braden) mine

This mine is located on a steep northwest-facing slope at an elevation of 2,100 to just over 3,300 m above sea level on the western slope of the Andes in central Chile, 72 km southeast of Santiago (Figs. 1 and 2). General geology, mineralization, hydrothermal alteration, and origin of the deposit is described by Howell and Malloy (1960) and Camus (1975). Hydrothermal alteration at El Teniente is

<table>
<thead>
<tr>
<th>Table 5. Concentration of K, Rb, and Sr in 43 Paleozoic to Tertiary Intrusive Rocks from Chile</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>Quartz diorite (7)</td>
</tr>
<tr>
<td>Granodiorite (22)</td>
</tr>
<tr>
<td>Quartz monzonite (12)</td>
</tr>
<tr>
<td>Granite (2)</td>
</tr>
</tbody>
</table>

( ) = Number of samples.
TABLE 6. Distribution of K and Rb in Fresh, Slightly Altered, and Moderately Altered Intrusive Rocks in Chile

<table>
<thead>
<tr>
<th>Rock Type</th>
<th>K%</th>
<th>Rb ppm</th>
<th>K%</th>
<th>Rb ppm</th>
<th>K%</th>
<th>Rb ppm</th>
<th>K%</th>
<th>Rb ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz diorite</td>
<td>1.23(6)</td>
<td>51(6)</td>
<td>2.05(10)</td>
<td>88(10)</td>
<td>3.07(2)</td>
<td>166(2)</td>
<td>4.26(2)</td>
<td>245(2)</td>
</tr>
<tr>
<td>Slightly altered</td>
<td>0.95(1)</td>
<td>43(1)</td>
<td>2.24(8)</td>
<td>93(8)</td>
<td>2.73(9)</td>
<td>110(9)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moderately altered</td>
<td>2.19(4)</td>
<td>74(4)</td>
<td>2.18(1)</td>
<td>106(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 One feldspar cloudy.
2 Both feldspars cloudy.
( ) = Number of samples.

Geology, mineralization, and alteration: The orebody mainly lies in massive, gently folded andesitic lavas of the lower member of the Farellones formation, but part is located in quartz diorite and dacite porphyry intrusions (Fig. 2) aligned in a north-south direction parallel to regional structures. Dacite porphyry cuts quartz diorite, but in some occurrences the dacite porphyry closely resembles the porphyritic facies of the quartz diorite, indicating that the two rock types may have a close genetic relationship (Howell and Malloy, 1960).

Volcanic and intrusive rocks are cut by the Braden pipe, a breccia-filled, circular pipe with surface diameter of 1,200 m which tapers with depth. Breccia fragments of andesite, quartz diorite, and dacite porphyry range in size from submicroscopic to over 1 m in diameter. Irregular intrusions of auto-breciated latite porphyry are restricted to the breccia pipe. The pipe and latite porphyry intrusions formed after the main period of mineralization.

The orebody at El Teniente surrounds the Braden pipe, with a maximum width of about 700 m on the east and north sides of the pipe. Ore occurs in andesite, quartz diorite, and dacite porphyry, and extends into the Braden pipe wherever mineralized fragments are abundant. The main stage of hypogene mineralization consists of chalcopyrite, pyrite, bornite, and molybdenite in a gangue of quartz, anhydrite, and chlorite. Sulfide zoning is well developed with bornite-chalcopyrite near the pipe grading outward into a zone of chalcopyrite-pyrite, and finally into pyrite with only minor chalcopyrite; total sulfide content decreases away from the pipe. Sulfides in stockworks and veinlets are common in andesite and quartz diorite. Disseminated sulfides, mainly bornite, are abundant in dacite porphyry. A leached capping 0 to 130 m thick overlies oxide and supergene enriched zones of variable thickness. Some supergene ore extends more than 900 m below the surface.

Hydrothermal alteration in andesite, quartz diorite, and dacite porphyry becomes less pervasive outward and away from the Braden pipe. Rock type has a marked effect on the alteration minerals assemblage that is developed.

Andesite near the pipe is flooded with fine-grained secondary biotite which comprises up to 50 percent of the rock. Biotite replaces original ferromagnesian minerals, and to a lesser extent also replaces plagioclase. Biotitic alteration grades outward into a propylitic assemblage of epidote, chlorite, and magnetite with minor pyrite, tourmaline, and biotite. The distinction between biotitic and propylitic alteration in andesite may be difficult, as both can appear fresh, dark green to black, and massive, the only distinguishing feature of the biotitic sample being veinlets of sulfide. The boundary between biotitic and propylitic alteration zones lies along the margin of the orebody.

Quartz diorite, adjacent to andesite which has undergone strong biotitic alteration, has been intensely altered to a quartz-sericite rock by complete destruction of plagioclase and ferromagnesian minerals. Secondary biotite may be present but is commonly partly altered to chlorite and sericite. This close association of quartz-sericite alteration in quartz diorite with biotitic alteration in andesite strongly suggests that both were produced by the same hydrothermal fluid, the differences being due largely to differences in composition of host rocks, that is, due to the higher activities of Mg and Fe and lower activity of K in andesite relative to quartz diorite. Outside the orebody quartz diorite is altered to a propylitic assemblage consisting of chlorite, albite, epidote, calcite, quartz, pyrite, and minor sericite.

Dacite porphyry contains locally pervasive sericitization and silicification of the feldspars and groundmass, but much of the intrusion appears to be relatively unaltered, although veinlets of bornite, quartz and secondary K-feldspar may be abundant. This rock type occurs only within the mine area and is cut by the Braden pipe, which suggests that dacite porphyry once formed a central core in the deposit area and was later destroyed during the explosive activity which led to the formation of the Braden pipe.
TABLE 7. Concentration of K, Rb, and Sr in Rocks at El Teniente

<table>
<thead>
<tr>
<th></th>
<th>K%</th>
<th>Rb ppm</th>
<th>K/Rb</th>
<th>Sr ppm</th>
<th>Rb/Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh andesite (12)</td>
<td>1.46</td>
<td>43</td>
<td>447</td>
<td>494</td>
<td>0.09</td>
</tr>
<tr>
<td>Propylitic zone (29)</td>
<td>1.53</td>
<td>85</td>
<td>181</td>
<td>331</td>
<td>0.26</td>
</tr>
<tr>
<td>Biotitic zone (54)</td>
<td>2.70</td>
<td>155</td>
<td>178</td>
<td>390</td>
<td>0.39</td>
</tr>
<tr>
<td>Hypogene zone (22)</td>
<td>2.69</td>
<td>158</td>
<td>174</td>
<td>234</td>
<td>0.68</td>
</tr>
<tr>
<td>Leached capping (4)</td>
<td>3.26</td>
<td>154</td>
<td>216</td>
<td>29</td>
<td>5.31</td>
</tr>
<tr>
<td>Fresh quartz diorite (7)</td>
<td>1.19</td>
<td>50</td>
<td>261</td>
<td>475 (5)</td>
<td>0.12</td>
</tr>
<tr>
<td>Quartz diorite (Propylitic alteration) (3)</td>
<td>2.11</td>
<td>113</td>
<td>187</td>
<td>363 (2)</td>
<td>0.30</td>
</tr>
<tr>
<td>Quartz diorite (Quartz-sericite alteration)</td>
<td>3.43</td>
<td>157</td>
<td>218</td>
<td>393</td>
<td>0.40</td>
</tr>
<tr>
<td>Hypogene zone (11)</td>
<td>3.36</td>
<td>156</td>
<td>216</td>
<td>109</td>
<td>1.43</td>
</tr>
<tr>
<td>Supergene zone (4)</td>
<td>5.83</td>
<td>179</td>
<td>325</td>
<td>253</td>
<td>0.71</td>
</tr>
</tbody>
</table>

( ) = Number of samples.

Other abundant secondary minerals at El Teniente include tourmaline and anhydrite. Tourmaline is most abundant as matrix between fragments near the margin of the Braden breccia, and occurs in lesser amounts in biotitic and propylitic zones in andesite. Anhydrite, second only to quartz in abundance in all host rocks, occurs in veinlets and disseminations, producing a massive, hard rock. Anhydrite undergoes supergene hydration to gypsum or is dissolved, producing a rather porous, soft rock well suited to block-caving mining methods.

Chalcopyrite veinlets of the main stage of mineralization in andesite generally have narrow bleached margins produced by alteration of secondary biotite to chlorite and/or sericite. Thus, biotitic and propylitic alteration is thought to be a preore phenomenon, perhaps related to the intrusion of quartz diorite (Howell and Malloy, 1960). However, biotite often forms at relatively high temperature during hydrothermal alteration and may be subject to retrograde alteration during the waning stages of hydrothermal activity, resulting in chloritization or bleaching of biotite. The common association of biotitic alteration and mineralization at other porphyry copper deposits and the location of the biotitic-propylitic boundary at the margin of the ore deposit at El Teniente suggest that the mineralization and biotitic alteration are related.

K-Rb-Sr geochemistry: Results of 121 analyses for K, Rb, and Sr in andesite are shown in Table 7 and Figure 4. Rb in andesites of the propylitic zone (mean, 85 ppm) is twice that of background (43 ppm), and an even larger increase over background is present in biotitic alteration (155 ppm). The latter represents almost a fourfold increase relative to fresh andesite of the Farellones formation. K contents of the fresh and propylitized andesites are very similar (1.46 and 1.53 percent, respectively), but K in the biotite zone is almost double (2.70 percent) that in the propylitic zone. This results in a decrease in the K/Rb ratio from 447 for fresh andesite to 181 and 178 for the propylitic and biotite zones, respectively.

Figure 5 shows the concentration of Rb in samples taken along cross sections AB and CD (see Fig. 2) through the orebody and into the zone of propylitic alteration at El Teniente. The highest values occur near the Braden pipe, with significant decrease near the transition from biotitic to propylitic alteration. Note that Rb values are consistently above background values even 400 m from the orebody.

Similar K/Rb ratios in the propylitic and biotitic zones may indicate that, although little if any K was added to the propylitic rocks, K minerals in both zones were able to equilibrate with the same Rb-rich hydrothermal fluid. Both K and Rb were partially removed from the hydrothermal fluid, producing fine-grained biotite in the inner, higher temperature zone of alteration; K minerals, such as minor biotite and sericite, present in the lower temperature, outer zone of propylitic alteration were able to equilibrate with a fluid which still contained an abnormally high concentration of Rb relative to K, but the K content in the rocks did not increase. If this interpretation is correct, similar K/Rb ratios would support the contention that the biotitic and
Fig. 4. Frequency distribution of K, Rb, and Sr in rocks at El Teniente.
propylitic alteration were contemporaneous, and were due to reaction of andesite with the same hydrothermal fluids at different temperatures.

A study of Rb distribution at the Ogofau Gold Mine, southern Wales, shows that in 84 percent of samples from the zone of mineralization enhancement of Rb is greater than three standard deviations (30 ppm) over background values (Al-Atia and Barnes, 1974). No accompanying change in K content was noted. This may also represent an equilibration between Au-bearing, Rb-rich hydrothermal fluid and K minerals in the rock.

A general correlation between Rb concentration and Cu mineralization exists at El Teniente with Rb and Cu values highest near the Braden pipe. Concentrations of both elements abruptly decrease at the transition from the biotitic zone into the zone of propylitic alteration. However, a close relationship between Rb and Cu in the individual samples was not observed. This may be due in part to the method of sampling. The 500-g rock samples are probably large enough to be representative for the pervasive wall-rock alteration but are not representative for Cu which is usually confined to veinlets. Therefore, Cu concentration depends on abundance of veinlets in the relatively small sample, and large samples are required to determine if the Rb and Cu contents are closely related.

Andesite in the propylitic zone contains about one-third less Sr (331 ppm, Table 7) than in fresh andesites from the Farellones formation (494 ppm). Sr, which substitutes for Ca in Ca minerals, was apparently removed during chloritization of pyroxene and partial breakdown of plagioclase. Some Ca and Sr was retained in epidote and tourmaline.

Phyllic alteration commonly leads to removal of a large part of the Ca and Sr from a rock. Plagioclase, and ferromagnesian minerals that contain Ca, can be completely replaced by a Ca-free assemblage of quartz, sericite, and pyrite. Ca and Sr can also be removed during potassic alteration due to the replacement of plagioclase by K-feldspar and/or the replacement of pyroxene or amphibole by biotite. At El Teniente, extensive removal of Sr did not occur in the biotitic zone (390 ppm). During biotitic alteration, original Ca minerals were replaced, but much of the Ca and Sr is retained in the abundant anhydrite.

Supergene alteration of andesite in the biotite zone does not change the K or Rb content of the rock (Fig. 4 and Table 7), but Sr decreases from a mean of 390 ppm to 234 ppm. Anhydrite, minor tourmaline, and some relict plagioclase are the only Ca-Sr minerals in the biotitic zone. Of these anhydrite is most susceptible to supergene alteration. Anhydrite is hydrated to gypsum which is partially dissolved in
slightly altered samples. All gypsum is removed, sulfides oxidized, and plagioclase replaced by clay minerals in strongly altered rocks. As gypsum is easily removed during supergene alteration, Sr content of the orebody at El Teniente can be used as a sensitive indicator of supergene activity.

Four highly weathered samples of andesite from leached capping above the ore zone contain very little Sr (mean, 29 ppm) in contrast to unweathered samples from the biotitic zone (390 ppm). Rb in the leached capping and the underlying ore zone is identical (154 ppm). Thin section and X-ray diffraction analyses show that weathered andesites contain quartz, sericite, chlorite, and minor biotite. Feldspar is not present. Acid water produced by weathering of sulfides apparently was able to extract nearly all Ca and Sr from plagioclase and ferromagnesian minerals, while K and Rb were retained in sericite and/or illite and minor amounts of unweathered biotite. Thus, Rb may be a useful indicator of the original potassic alteration in areas where hydrothermal alteration has been masked by effects of strong supergene processes.

The difficulty in obtaining fresh samples from intrusive rocks at porphyry copper deposits requires that background values be taken from unaltered rocks not related to areas of mineralization (Tables 2 and 5). K, Rb, and Sr values for 18 samples of quartz diorite and 13 samples of dacite porphyry at El Teniente (Table 7 and Fig. 4) are similar to those in altered andesites. Background values for Rb in quartz diorite and dacite porphyry are 50 and 44 ppm, respectively. A twofold increase in Rb for quartz diorite (mean, 113 ppm) occurs in the propylitic zone, and approximately a threefold increase for quartz diorite (157 ppm) and dacite porphyry (140 ppm) in the zone of quartz-sericite alteration. Supergene alteration does not appear to affect the Rb content in these rocks. Frequency distributions for K, Rb, and Sr in andesite (Fig. 4) show well-defined peaks, but values are scattered in quartz diorite and dacite porphyry. This is probably due to insufficient sampling of the intrusive rocks.

The Rio Blanco and Los Bronces mines

The Rio Blanco and Los Bronces (Disputada) deposits are located about 100 km due north of El Teniente in similarly high rugged terrain (Fig. 1). They are 1,500 m apart and are probably genetically related.

Geology, mineralization, and alteration: Five major rock units at Rio Blanco are andesitic volcanic host rocks intruded by a granodioritic massif, a quartz porphyry dike, a rhyolite plug, and bodies of tourmaline breccia (Urqueta, 1969, fig. 5). Modal analysis indicates that most of the intrusion is transitional between granodiorite and quartz monzonite. A north-south-trending quartz porphyry dike which cuts the volcanic and granodioritic rocks contains phenocrysts of quartz and feldspar in an aphanitic groundmass. Original composition of the rock is unknown because of almost complete replacement of feldspar by calcite and sericite. The northern end of the quartz porphyry dike is cut off by a rhyolite plug with the shape of a downward-tapering cone. Massive rhyolite in this plug grades upward into flow-banded rhyolite and welded tuff. Breccia at Rio Blanco occurs as irregularly shaped bodies along the contact between the andesite and quartz porphyry dike, and contains angular to poorly rounded fragments of both rock types in a matrix.
of tourmaline and quartz. Mineralization is present in the fragments and the matrix.

Most ore at Rio Blanco is confined to an andesitic roof pendant in the granodioritic intrusion. Light gray "hybrid rock", consisting of quartz, sericite, and minor tourmaline, is developed at the contact between andesite and granodiorite. The margin of the orebody is an assay wall on the west and south in granodiorite host rock. Ore is abruptly cut off on the east and north by the quartz porphyry dike and rhyolite plug, respectively. Neither of these two rock types is mineralized.

Mineralization as disseminations and veinlets consists of pyrite, chalcopyrite, and martite, with minor magnetite, specularite, and molybdenite. Gangue minerals are mainly quartz and sericite, with minor tourmaline, chlorite, and biotite. Supergene enrichment is rare; secondary copper sulfides are less than 2 percent of the ore.

The Los Bronces orebody, located approximately 1,500 m west of Rio Blanco, is confined to a breccia pipe cutting granodiorite (Alfaro, 1970). The pipe, forming an inverted cone having surface dimensions of 1,200 by 450 m and a vertical axis of over 700 m, contains angular fragments of granodiorite set in a matrix of tourmaline, quartz, pyrite, chalcopyrite, specularite, and minor molybdenite and magnetite.

Two zones of hydrothermal alteration at Rio Blanco are an inner zone of quartz-sericite-pyrite containing minor biotite, coinciding with the orebody, and an external zone of propylitic alteration consisting of calcite, chlorite, epidote, and minor sericite. Silicification and tourmalinization are important in upper levels of the mine and coincide with high-grade ore.

Hydrothermal alteration at Los Bronces consists of intense silicification and sericitization, and is confined to the fragments in the breccia. The granodioritic rocks surrounding the pipe are relatively fresh; the only evidence of alteration is replacement of ferromagnesian minerals by chlorite and trace amounts of sericite in plagioclase.

K-Rb-Sr geochemistry: Sampling at Rio Blanco and Los Bronces was much less detailed than at El Teniente. Only 18 samples of andesite were collected at Rio Blanco: two from the propylitic zone and 16 from the quartz-sericite zone associated with the orebody. A total of 21 samples were taken from the quartz monzonite-granodioritic intrusion: nine fresh samples, three from the propylitic zone, four from the orebody at Rio Blanco, and five from the rock fragments in the breccia pipe at Los Bronces.

High Rb values are found in the quartz-sericite alteration zone associated with the orebodies at Rio Blanco and Los Bronces (Table 8 and Fig. 7). At Rio Blanco, andesite samples with quartz-sericite alteration contain 140 ppm Rb, which is more than a threefold increase above the mean background value of 43 ppm. Altered granodioritic host rocks at Rio Blanco and in breccia fragments at Los Bronces contain 144 ppm and 191 ppm Rb, respectively. This represents less than a twofold increase over the high background value of 108 ppm.

The Rb content in the zone of propylitic alteration was not determined because of insufficient sample coverage. However, the mean Rb content in two samples of andesite from this zone is 58 percent above background value. This suggests that Rb enrichment extends beyond the zone of quartz-sericite alteration.

K in andesite associated with the orebody at Rio Blanco shows a large increase from 1.46 percent for fresh andesite to 4.80 percent in the quartz-sericite zone; the K/Rb ratio decreases from 447 to 340. Similarly, in granodioritic rocks from both mines, K increases from 2.66 percent in fresh rocks to 4.06 percent in the quartz-sericite zone. The K/Rb ratio decreases slightly from 260 to 242.

<table>
<thead>
<tr>
<th></th>
<th>K%</th>
<th>Rb ppm</th>
<th>K/Rb</th>
<th>Sr ppm</th>
<th>Rb/Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh andesite</td>
<td>1.46</td>
<td>43</td>
<td>447</td>
<td>494</td>
<td>0.09</td>
</tr>
<tr>
<td>Andesite (Propylitic zone)</td>
<td>1.85</td>
<td>68</td>
<td>276</td>
<td>235</td>
<td>0.29</td>
</tr>
<tr>
<td>Andesite (Ore zone)</td>
<td>4.80</td>
<td>140</td>
<td>340</td>
<td>71</td>
<td>1.97</td>
</tr>
<tr>
<td>Fresh intrusives</td>
<td>2.66</td>
<td>108</td>
<td>260</td>
<td>550(7)</td>
<td>0.20</td>
</tr>
<tr>
<td>Intrusives (Propylitic zone)</td>
<td>3.05</td>
<td>127</td>
<td>239</td>
<td>408(2)</td>
<td>0.31</td>
</tr>
<tr>
<td>Intrusives (Quartz-sericite zone)</td>
<td>4.06</td>
<td>170</td>
<td>242</td>
<td>64(4)</td>
<td>2.24</td>
</tr>
<tr>
<td>Rio Blanco</td>
<td>3.60</td>
<td>144</td>
<td>254</td>
<td>64</td>
<td>2.42</td>
</tr>
<tr>
<td>Los Bronces</td>
<td>4.42</td>
<td>191</td>
<td>234</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 Granodiorite-quartz monzonite.
2 Mean for quartz-sericite alteration at Rio Blanco and Los Bronces.
( ) = Number of samples.
A substantial decrease in Sr in altered rocks exists at Rio Blanco and Los Bronces, despite the fact that supergene alteration is negligible at both mines. Sr decreases from 494 ppm in fresh andesite to 235 ppm in the zone of propylitic alteration, to only 71 ppm in the quartz-sericite zone. A similar decrease in Sr is noted in granodioritic rocks, with 550 ppm in the fresh rocks, 408 ppm in the zone of propylitic alteration, and 64 ppm in the quartz-sericite zone. As samples collected at Rio Blanco and Los Bronces show no evidence of supergene alteration, the strong leaching of Sr at the two mines is apparently due to hypogene alteration.

The Rb/Sr ratio should be an even more sensitive guide to types of hydrothermal alteration commonly associated with ore zones in porphyry copper deposits than either Rb or Sr separately. As the Rb content increases toward the orebody, Sr decreases; thus the Rb/Sr ratio increases at a rapid rate toward the ore zone. This is especially true where Ca and Sr are not retained in an alteration product such as anhydrite. The Rb/Sr ratio in the andesite at Rio Blanco increases from 0.09 in fresh rock to 0.29 and 1.97 in the propylitic and quartz-sericite zones, respectively (Table 8). The latter value represents a 22-fold increase over the background value.

Care must be taken in interpreting the significance of Rb/Sr ratios. A large increase in the Rb/Sr ratio can be produced in rocks that have not been hydrothermally altered by means of normal weathering processes through extensive leaching of Ca and Sr relative to Rb. Rb/Sr ratios may yield useful

---

**Fig. 7.** Frequency distribution of K, Rb, and Sr in rocks at Rio Blanco and Los Bronces.
information only where supergene effects have been minimal because substantial amounts of Sr are usually removed from the zones of propylitic and argillic (kaolinite, montmorillonite, sericite) alteration. This produces a wide Rb/Sr anomaly adjacent to the orebody, thus increasing the target for exploration.

Comparison of the El Teniente and Rio Blanco deposits

The El Teniente and Rio Blanco deposits show several similar features:

— Both are associated with intrusive rocks of intermediate composition, although those at Rio Blanco are slightly more siliceous and have higher Rb background values than at El Teniente.
— The intrusions cut similar host rocks (andesites of the Farellones formation).
— Both deposits are cut by siliceous, postmineralization intrusive-extrusive rocks (latite porphyry in the breccia pipe at El Teniente and quartz porphyry and rhyolite at Rio Blanco).
— Mineralization in both deposits consists of chalcopyrite, pyrite, and minor bornite in veinlets and disseminations in andesite and intrusive rocks.
— Tourmaline breccias are associated with both deposits.
— The concentration of Rb in the altered rocks associated with the ore is three to four times the background value for the unaltered andesite. A smaller increase was noted in the zone of propylitic alteration.
— Both deposits are in similar geographic and topographic settings near the present axis of the Andes.

Despite the above-mentioned similarities, there are important differences between the two deposits:

— Lack of significant supergene enrichment at Rio Blanco (98 percent of the mineralization is of hypogene origin).
— A substantially greater addition of K to the rocks in the ore zone at Rio Blanco than at El Teniente.
— Biotite and anhydrite are scarce in the ore zone at Rio Blanco.

Differences in abundance of K, Rb, and Sr in andesites at the two mines may be explained by comparing alteration mineral assemblages. A biotite-anhydrite assemblage is common in the ore zone at El Teniente, and quartz-sericite with only minor biotite and little or no anhydrite is common in ore at Rio Blanco. The latter assemblage indicates stronger hydrolytic leaching at Rio Blanco than at El Teniente. At Rio Blanco the activity of H⁺ ions in the hydrothermal fluid was sufficiently high to leach out much of the Fe and Mg from the andesite, preventing the formation of abundant biotite. Leaching of Ca from plagioclase, as indicated by the low Sr values, precluded the formation of anhydrite. However, the intensity of hydrolytic activity was not sufficiently high to cause the removal of K and Rb. Sericite, rather than kaolinite, is the stable alteration product.

Summary and Conclusions

The following conclusions, based on the study at El Teniente, Rio Blanco, and Los Broncos, may also apply at other porphyry copper deposits:

1. Rocks that have undergone potassic or sericitic alteration also show a two- to threefold increase in Rb and have low K/Rb ratios. As these types of alteration characteristically accompany mineralization in porphyry copper deposits, a study of the distribution of Rb may be useful to locate favorable alteration zones for porphyry copper exploration. Strongest enrichment is found in mafic host rocks, which have low Rb background values, though anomalies can also be detected in rocks as siliceous as quartz monzonite.

Rb tends to be preferentially concentrated in micas relative to K-feldspar, and Rb prefers biotite to muscovite (Heier and Billings, 1970). Thus, relatively low K/Rb anomalies should exist where the alteration product is biotite. This is supported by the data from El Teniente, where the K/Rb ratio is very low in andesites which have undergone biotitic alteration (178), is somewhat higher in the quartz diorite which has undergone quartz-sericite alteration (218), and is highest in the dacite porphyry which has been altered to a quartz-sericite-K-feldspar assemblage (268).

2. A twofold increase in Rb in the propylitic zone at El Teniente produces an anomaly that extends more than 400 m beyond the margin of the orebody. No corresponding increase in K was observed. The Rb anomaly represents an enlarged target enclosing the zones of alteration commonly associated with porphyry copper mineralization. It would be interesting to compare the distribution of Rb in the propylitic zone at El Teniente with that of a propylitic zone around an intrusion not associated with significant Cu mineralization or a centrally developed zone of K enrichment.

3. Weathering does not affect the distribution of Rb in rocks from the leached capping at El Teniente. Webber and Jellema (1965) compared K and Rb
concentrations in soils and their parent rocks at Mont St. Hilaire, Quebec, and recorded a K-soil/K-rock ratio of 0.54, and a Rb-soil/Rb-rock ratio of 1.07, which indicates that almost one-half of the K was removed during weathering while Rb was slightly concentrated. Goldschmidt (1954) noted that during weathering and soil formation Rb is more firmly held than K both by absorption and by cation exchange. Due to this immobility of Rb, weathering of the potassic zone in porphyry copper deposits should not destroy the Rb anomaly. Thus, distribution of Rb could be a useful tool to locate potassic alteration zones in areas of tropical weathering, for example, in the southwest Pacific and Central America. There is a critical need for research into the distribution of Rb in soils above porphyry copper deposits, but this must be done before the surface has been disturbed by mining operations.

4. Addition of Rb and removal of Sr during hypogene alteration can produce high Rb/Sr anomalies which extend out through all zones of hydrothermal alteration, thereby increasing the size of the exploration target. However, care must be taken in interpreting the significance of Rb/Sr anomalies because they may simply indicate extensive removal of Sr during normal weathering processes.

5. Contouring Rb values may be useful for quantitative mapping of the extensiveness of K metasomatism.

6. Anhydrite is readily dissolved and removed by acid meteoric waters. In deposits where anhydrite is an abundant hypogene alteration product, Sr depletion can be used as a quantitative guide to the degree of supergene activity.

Every zone of potassic alteration is not mineralized. However, most porphyry copper deposits are closely associated with potassic alteration, and because of this, potassic zones are considered to be favorable areas for mineral exploration. Rb may be a useful aid in locating these favorable zones, especially where the hypogene alteration has been masked by weathering.

Acknowledgments

The authors wish to thank the geological staff at El Teniente, Rio Blanco, and Los Bronces, especially Messrs. A. Enríquez, I. Urqueta, and G. Marcel, for their generous assistance during field work at the three mines. Special thanks and appreciation are extended to D. Garrett for the AAS analyses, to R. Goodman and C. de la Fuente for XRF work, and to J. D. Lowell and J. M. Guilbert for critically reviewing the manuscript. This paper is published with the permission of Sociedad Minera El Teniente, Compañía Minera Andina, and Compañía Minera Disputada de Las Condes.

G. A. A.
DEPARTMENT OF GEOLOGY
UNIVERSITY OF OTTAWA
OTTAWA, ONTARIO, CANADA K1N 6N5

J. O.
UNIVERSIDAD DEL NORTE
CASILLA 1280
ANTOFAGASTA, CHILE

J. ARIAS
INSTITUTO DE INVESTIGACIONES GEOLOGICAS
CASILLA 10465
SANTIAGO, CHILE
APRIL 20, NOVEMBER 3, 1976

REFERENCES


Armbrust, G. A., Oyarzun Munoz, J., and Arias Farias, J., 1971, Rubidium as a guide to ore at El Teniente (Braden), Chile [abs.]: Econ. Geol., v. 66, p. 977.

Camus, P., 1975, Geology of the El Teniente orebody with emphasis on wall-rock alteration: Econ. Geol., v. 70, p. 1341-1372.


Howell, F. H., and Molloy, J. S., 1960, Geology of the Braden orebody, Chile, South America: Econ. Geol., v. 55, p. 863-905.


Ruiz, C., 1965, Geología y yacimientos metalíferos de Chile: Instituto de Investigaciones Geológicas, Santiago, Chile.