Geochemical Studies of Upper Cenozoic Igneous Rocks from the Altiplano of Antofagasta, Chile

Moyra Gardeweg*, Shunso Ishihara**, Yukihiro Matsuhisa***, Ken Shibata**** and Shigeru Terashima****

GARDEWEG, MOYRA, ISHIHARA, Shunso, MATSUHISA, Yukihiro, SHIBATA, Ken and TERA-SHIMA, Shigeru (1984) Geochemical studies of Upper Cenozoic igneous rocks from the Altiplano of Antofagasta, Chile. *Bull. Geol. Surv. Japan*, vol. 35(11), p. 547–563.

Abstract: Magnetic susceptibility, tin, rubidium and strontium contents, and oxygen and strontium isotopic ratios were measured for Upper Cenozoic igneous rocks from the Guatiquina area, Altiplano of Antofagasta, northern Chile. The rocks are mainly andesites, dacites and ignimbrites of calc-alkaline series, and their equivalents of subvolcanic rocks. The analytical results were examined in view of contribution of crustal material to the magmas at a distructive continental plate margin.

Magnetic susceptibility of the studied rocks are mostly between 600 and $1,600 \times 10^{-5}$ SI, corresponding to the lower half of the range for the magnetite-series rocks. An El Laco andesite, which contains many phenocrysts of polygonal and some cubic magnetite, has the highest value of $2,066 \times 10^{-5}$ SI. Some of the rocks, including both effusive and subvolcanic rocks, from the area north of latitude 23°S may possibly belong to the ilmenite-series.

The Sn contents of the rocks are generally as low as 1.1 to 3.7 ppm. Sn-rich igneous rocks equivalent to "tin-granite" do not widely exist in the area. Therefore, southwestern prolongation of the Bolivian tin belt to this area is not plausible.

The δ^{18} O values and initial 87 Sr/ 86 Sr ratios of the rocks range from +7.8 to +11.2 per mil and 0.7069 to 0.7131, respectively. A positive correlation is observed between the 18 O/ 16 O and 87 Sr/ 86 Sr ratios, while the 87 Sr/ 86 Sr ratios increase with decreasing in Sr concentration. These results suggest involvement of 18 O- and 87 Sr/ 86 Sr ratio toward north is observed in the studied area with the highest values at around 23 °S. This accords with that the ilmenite-series affinity of the rocks is observed in the area north of 23 °S. Contribution of crustal material to the andesitic magmas would be large in the area around 23 °S. This may be attributed to either the crustal thickness under the area or tectonic environment in which the magmas have formed, or both.

Introduction

Late Cenozoic volcanism of the Andean orogenic belt is restricted to three zones: a

northern zone in southern Colombia and Ecuador ($5^{\circ}N-2^{\circ}S$), a central zone in southern Peru, southwestern Bolivia, northern Chile and northwestern Argentina ($16^{\circ}-28^{\circ}S$), a southern zone in southern Chile and Argentina ($33^{\circ}-52^{\circ}S$). The differences in bulk and trace element compositions among these zones suggest that the magma generation processes are much more complicated in the Andean continental plate margin than those along intra-oceanic island arc systems.

^{*} Servicio Nacional de Geología y Minería, Casilla 10465, Santiago, Chile

^{**} Research Planning Office, *** Mineral Deposits Department, **** Geochemistry & Technical Services Department, Geological Survey of Japan, Higashi 1-1-3, Yatabe, Tsukuba, Ibaraki, 305 Japan

Bulletin of the Geological Survey of Japan, Vol. 35, No. 11

The Central Andes where the studied area is located is characterized by two main groups of volcanic rocks: composite stratovolcanoes of mainly andesitic-dacitic composition and large volume of ignimbrite sheets of dacitic and rhyolitic composition. As in most parts of the Andes, the volcanics of this zone are mainly of calc-alkaline association, but in the north of latitude 26°S parallel to the Chile-Peru trench, there is a continuous gradation toward east from calc-alkaline rocks to a shoshonitic volcanic association (MUNIZAGA and MARINOVIĆ, 1979; DERUELLE, 1981). Together with this gradation, the volcanics vary systematically in their chemical and isotopic compositions with SiO₂, K₂O, Rb, ⁸⁷Sr/ ⁸⁶Sr increasing from west to east (HARMON et al., 1981). The Central Andes volcanics are generally enriched in K₂O, Rb, ⁸⁷Sr/⁸⁶Sr and ¹⁸O, as compared with the Upper Cenozoic volcanic rocks of both northern and southern Andes.

Volcanism of the Central Andes has been for a long time a matter of controversy with regard to the petrogenesis of these rocks, especially in relation to the parental magma under the destructive plate margin along which they are developed. During the last five years, the number of trace element and isotopic studies of these rocks has markedly increased. Nevertheless, the reported ⁸⁷Sr/ ⁸⁶Sr ratios and δ^{18} O values differ not only between those of the northern and southern Andes (FRANCIS et al., 1977; HAWKESWORTH et al., 1979; MUEHLENBACHS and STERN, 1980), but also within nearby areas in the Central Andes (HAWKESWORTH et al., 1982), and even within the same volcanic complex (JAMES et al., 1976; FRANCIS et al., 1980).

Most of these studies have been done with samples of isolated points, frequently studying one or two volcanic complexes. They may represent a very small portion of the large volcanic chain of the Central Andes. Their apparently contradictory results and conclusions lead us to think necessity of additional and more detailed works in the volcanic chain.

The present paper reports new geochemical data of Upper Cenozoic igneous rocks of the Guatiquina area, in the High Andes of Antofagasta, Chile, including andesites, ignimbrites, glassy dacite-rhyolites and subvolcanic rocks. Some of them were taken from isolated bodies but others, like the ignimbrites and porphyries of Cerros Chamaca, Arenoso, Chivato Muerto and Corral de Coquena, appear to be genetically related. Magnetic susceptibility and tin content of all the available samples were determined, because of the proximity of the studied area to the "Bolivian tin belt" and their distinct relationship to tin ore deposits of granitic affinity (ISHIHARA and TERASHIMA, 1977). Age and petrochemical characteristics of the subvolcanic rocks of the studied area made us think of a possibility of finding a southwestern prolongation of the tin belt.

Geological Setting of Central Andes

The widely extended Upper Cenozoic volcanic rocks of the Central Andes hide the previous geological history of the area. The volcanic activity has been developed along the Western Cordillera and the Altiplano. The main centers of eruption are along the borders between Chile and Bolivia and Chile and Argentina (Fig. 1). Toward the east, eruptions took place all the way across to the foothills of the Eastern Cordillera in Peru, Bolivia and Argentina.

The Upper Cenozoic volcanic materials, together with some sedimentary clastic continental series, have been deposited over strongly folded, faulted and eroded Mesozoic and Lower Cenozoic rocks (LAHSEN, 1982). Few outcrops of Precambrian rocks have been found under younger rocks in the volcanic chain of southern Peru, Bolivia and northern Chile (PACCI *et al.*, 1980), while in northern Argentina large outcrops of Precambrian and Lower Paleozoic sedimentary and igneous rocks underlie and surround the young volcanic rocks. The occurrence of Precambrian rocks west of the volcanic belt in the Peruvian

Geochemical Studies of Upper Cenozoic Igneous Rocks (Gardeweg et al.)



Fig. 1 Distribution of Late Cenozoic volcanic rocks in the Central Andes between latitudes 16° and 30° south with the localities of igneous bodies isotopically studied. Compiled from Mapa Geologico de Chile, 1:1,000,000 (1980), Mapa Geologico de Bolivia, 1:1,000,000 (1078), Mapa Geologico de Argentina, 1:2,500,000 (1982), ALLMENDINGER et al. (1983) and JAMES et al. (1976).



Bulletin of the Geological Survey of Japan, Vol. 35, No. 11

Fig. 2 Bolivian tin belt (shaded area) and polymetallic Ag-Pb-Sn-Sb-Cu mineralizations (triangles) occurring to the south. After GRANT *et al.* (1976).

coast, and east of it, under the Bolivian Altiplano suggests that the volcanic chain of the Central Andes is underlain by Precambrian and/or Paleozoic "continental" crust (COBBING and PITCHER, 1972 in SILLITOE, 1972; COIRA *et al.*, 1982; ALLMENDINGER *et al.*, 1983). The thickness of this crust under the volcanic centers is of approximately 70 km in southern Peru and northern Chile, where the Cenozoic volcanics rest on the central "keel" of the Andes (HARMON *et al.*, 1981, Fig. 1).

Although the Upper Cenozoic volcanic products of Central Andes are considered as one geological unit (Fig. 1), N–S variations in the onset, evolution, intensity and lithology of the activity are locally observed along the volcanic belt (LAHSEN, 1982). These variations and other major tectonic changes along the Cordillera de los Andes correlate with changes of the subduction zone determined by offsets and changes in dip of the seismic zone (SWIFT and CARR, 1974). SILLITOE (1974) proposed that the longitudinal subdivisions of Chile and their boundaries are comparable to the transverse geological features in Japan and are also coincident with discontinuities on the underlying deep seismic zone and reflect transverse boundary zones between separate segments of oceanic lithosphere which are subducted as individual units, perhaps even at different rates.

The volcanic activity of the Central Andes shows a continuous development since Miocene until today (LAHSEN, 1982). It has been characterized by the eruption of extensive sheets of ignimbrites and the development of large composite stratovolcanoes of approximately the same age. There are also small intrusions of acidic subvolcanic bodies that



Fig. 3. Geological map and sample localities of the studied area. Based on GARDEWEG Y RAMIREZ (in press) and RAMIREZ y GARDEWEG (1982).

are insignificant in volume but are interesting because of their relation with some important mineral deposits (*e.g.*, Bolivian tin porphyries). At Poquis near the Chile-Argentina border, polymetallic mineralization (Sb–Sn– Ag–Mn–Pb–Cu) is known associated with a Miocene rhyolitic porphyry (TRAVISANY and DIAZ, 1978). Similar mineralization is also known to occur in the Argentine side (Fig. 2).

Geology and Sample Description

The Guatiquina area is located in the Central Andes in the Altiplano (or Puna) of Antofagasta, Chile (Fig. 3). It is formed mainly of volcanic rocks of Upper Tertiary, under which only small outcrops of older rocks are exposed in erosion windows. Marine clastic sediments of Ordovician age crop out near the Chilean-Argentinian border in the Poquis area (MARINOVIĆ, 1979), south of the Curutu volcano (MARINOVIĆ et al., 1976) and northwest of the Guaitiquina Pass (GARCIA et al., 1962, Fig. 3). Younger marine sediments of Cretaceous age and continental sediments of Tertiary age have also been recognized (GARDEWEG and RAMI-REZ, in press).

The Upper Cenozoic volcanics can be divided into three main rock types: ignimbrites as very extensive sheets, lavas associated with stratovolcanoes and small eruptive centers, and subvolcanic porphyries. They are mainly andesites and dacites that belong to calc-alkaline association although the easternmost samples (Fig. 3) present chemical characteristic similar to those of shoshonitic association (MUNIZAGA and MARINOVIĆ, 1979; GARDEWEG and RAMIREZ, in press).

The ignimbrites have Pliocene ages $(4.1 \pm 0.4 \text{ Ma}; 4.5 \pm 0.1 \text{ Ma}; 4.8 \pm 0.6 \text{ Ma}; \text{K-Ar}$ on biotites) and dacitic composition (GARDE-WEG and RAMIREZ, in press). In general they have big phenocrysts of quartz, plagioclase, biotite and usually some hornblende, pyrox-enes,, sphene, zircon, opaque minerals and pumice fragments of different sizes and shapes.

Among the stratovolcano-related lavas, two

big groups can be recognized: 1) andesites, 2) glassy rhyolites and dacites. The andesites have variable amounts of plagioclase and pyroxene phenocrysts, opaques and apatite as minor mineral phases. The older andesites (GMC-16) also have quartz, hornblende and biotite phenocrysts. In the Jachi volcano the andesites have big rounded quartz xenocrysts and pyroxene clots. The andesites from the El Laco volcano have opaques as phenocrysts and amygdules of massive chalcedony (?). The andesites of the Huailitas volcano occasionally contain big olivine phenocrysts with reaction rim and plagioclasepyroxene-opaques clots. The groundmass is usually glassy. Interbedded with these andesites some lithic welded tuffs are recognized (GARDEWEG, in prep.). The glassy dacites and rhyolites have Pliocene ages (GARDEWEG and RAMIREZ, in press) and they form domes like Cerro Chamaca and Loma Negra, lava domes like Cerro Bola (2.7 ± 0.2 Ma; K-Ar on biot.) or ring structures like Corral de Coquena (4.4 ± 0.5 Ma; K-Ar on biotite) and Cerros de Jarellon where black and brownish red obsidian also appears (Fig. 3).

The subvolcanic rocks are bodies of irregular shape, usually covered by ignimbrites or lavas. They are porphyries of dacitic and rhyolitic composition whose ages range from Upper Miocene to Lower Pliocene (Table 1) and they become older from west to east. In Poquis, near the Bolivian border, crops out the oldest quartz porphyry (12.88 ± 0.46 Ma; K-Ar on biotite) with big quartz, sanidine and biotite phenocrysts in a groundmass of quartz and feldspars with small crystals of zircon, apatite and opaques. It has metallic mineralization associated and is locally highly altered (MARINOVIĆ, 1979). West of Poquis, in the Cordones Quilapana and Ceja Alta $(8.0 \pm 2.0 \text{ Ma}; \text{ K-Ar on plagioclase})$ the subvolcanic outcrops are altered dacitic porphyries with big phenocrysts of plagioclase and biotite oxidized or replaced by chlorite and sericite aggregates. The groundmass is very fine and usually argillized. East of the Salar de Aguas Calientes (Fig. 3) crop out the youngest subvolcanic rocks $(4.8 \pm 0.2 \text{ Ma}; \text{K}-\text{Ar} \text{ on biotite})$. They are three subrounded bodies (Chamaca, Arenoso and Chivato Muerto) of porphyrytic texture and dacitic composition with big phenocrysts of quartz, plagioclase, red biotites and sphene in the groundmass of variable textures, but frequently spherulitic. The bodies are petrographically very similar to the ignimbrites of the area and probably genetically related.

Among these rocks, 35 samples mainly of lavas and porphyries were chosen for geochemical studies. Their locations are shown in Fig. 3 and then main characteristics and the analytical results are listed in Table 1.

Magnetic Susceptibility

Magnetic susceptibility of the available samples were measured by a Geoinstruments ky TH-1 meter and shown in SI unit (Table 1). Opaque minerals were observed on thin sections and three samples were studied on polished sections.

Magnetic susceptibility of the studied rocks are mostly between 600 and $1,600 \times 10^{-5}$ SI. This range is lower than that of the tholeiite series of the Hachijojima volcanic rocks and higher than that of the ilmenite-series and intermediate-series of the Setouchi volcanic





Bulletin of the Geological Survey of Japan, Vol. 35, No. 11

Sample No.	Rock type	Locality		Alteration	SiO ₂
GMC-1	Glassy dacite	Bola hill		Fresh	63.31
-3	Dacitic porphyry	Cordon Qui	lapana	Limonitization, chlorite, altered K-feld, calcite, silicification	
-5	Welded tuff (ignimbrite)	Pampa Red	onda	Fresh	61.61
-6	Rhyolitic banded and spherulitic glass	Jarellon hill	s	Limonite stained	73.09
-6-1	Rhyolitic obsidian	"		Locally devitrified	73.12
-7	Quartz porphyry (rhyol.)	Poquis		Oxidized biotite, groundmass slightly altered	71.49
-10	Dacitic porphyry	Cordon Ceja	a Alta(N)	Limonite, clay minerals and sericite in groundmass	67.78
-11	//	"		Slightly altered, similar to GMC-1	68.45
-12	"	"		Fresh plagioclase, chlorite in ground- mass	68.29
-16	Acidic andesite	//	(S)	Fresh, except for oxidized biotite	63.54
-19	Welded tuff (ignim.)	Arenoso hil	1 (N)	Relatively fresh, hematite	65.74
-20	Quartz porphyry (dacitic)	"		Relatively fresh, hematite	67.83
-21	//	"	(E)	Fresh	66.94
-22	Welded tuff with pumice fragments (ignim.)	"	(SE)	Fresh	66.88
-23	Quartz porphyry (dacitic)	Chivato Mu	erto hill	Altered in certain degree, very low	63.07
-24	Glassy dacitic dome	Chamaca hi	11 (NE)	Relatively fresh, hematite	69.15
-26	Welded tuff (ignim.)	"	(SE)	Fresh (but not completely)	68.28
-28	Spherulitic rhyolite	Corral de C	Coquena	Fresh	74.66
-121	Quartz porphyry	Poquis		~GMC-7	69.43
PG-119	Glassy dome	Loma Negra	a (N)	Oxidized biotites and pyroxenes	69.89
-126	Orthopyroxene and clino- pyroxene andesite	Jachi		Small amount of calcite and limonite stained on groundmass	59.49
-127	//	Jachi		Fresh, only small amount of chlorite	59.87
-200	Pyroxene andesite	Laco volcan	0	Fresh, except for some amygdules of undetermined composition	60.89
-211	Pyroxene and olivine andesite	Huailitas vo	lcano	Fresh	58.07
-212	Glassy pyroxene andesite	11		Small amount of limonite in fractures	62.57
-214	Acidic andesite	Morado hill	l	Oxidized hornblende	62.15
-217	Lithic welded tuff	Huailitas vo	lcano	Fresh, but with some rock fragments	68.00
-221	Orthopyroxene and clino- pyroxene andesite	"		Very small amount of chlorite in amygdules	59.85
-222	Pyroxene andesite	"		Fresh	62.72
-225	Lithic welded tuff (~ $PG-21$	7) ″		Fresh, but with some rock fragments	68.37
-227	Pyroxene andesite	"	(S)	Small limonite veins	60.17
-229	Pyroxene andesite	//		Abundant opaques	63.29
-230	Pyroxene andesite	"	(top)	Fresh	61.78
-231	Fe glassy andesite	//	(top)	Limonite stained	57.55
-234	Pyroxene andesite	"	(top)	Locally limonitized groundmass and pyroxene with opacitic rim	59.75

Table 1 Main characteristics and analytical date of Upper

* Age determined in other sample of the same body, ** Average, *** Assumed age.

K-Ar age (Ma)	Rb** (ppm)	Sr** (ppm)	⁸⁷ Rb/ ⁸⁶ Sr**	$({}^{87}{ m Sr}/{}^{86}{ m Sr})_{ m p}$ +	(87 S r/86 S r)o	δ ¹⁸ O _{SMOW} + (‰)	Sn + (ppm)	Magnetic suscept. ⁺ (×10 ⁻⁵) SI**
2.7±0.2(biot.)	125	269	1.35				2.0	1261
_					—		1.9	1115
4.1±0.4(biot.)	140	362	1.12				1.1	1409
_	222	154	4.17				3.4	225
_	215	130	4.79	_			3.7	245
12.88±0.46*	193+	255+	2.19	0.71348	0.71307	+10.9	1.7	589
_	156	324	1.39	_		+ 7.8	1.5	1186
	160	344	1.35			_	1.3	1417
$8.0{\pm}2.0(plag.)$	146	363	1.16			+ 7.5plag + 8.5w.r.	g. 1.3	1298
	117	562	0.60		—		1.6	1032
	108	573	0.55				1.9	24
(5.0)***	168+	273+	1.78	0.70988	0.70975	+ 8.6	1.5	135
_	163	266	1.77			_	2.0	37
4.5 ± 0.4 (biot.)	148+	294+	1.46	0.70951	0.70942	+ 8.6	2.0	950
4.8±0.2(biot.)	161	301	1.55	_	_	+10.2	1.7	134
(5.0)***	206+	220+	2.71	0.70973	0.70954	+11.2	1.9	164
4.8±0.6(biot.)	178	218	2.36	<u> </u>			2.3	1044
4.4±0.3(biot.)	188	105	5.18				2.3	447
$12.88 {\pm} 0.46{*}$	201	232	2.51		_		1.6	732
	134	240	1.62	<u> </u>	—	—	1.6	164
4.9 ± 0.4 (w. r.)	89	380	0.68	—	_		1.2	
(4.9)***	83.1+	410+	0.587	0.70695	0.70691	+ 8.3	1.8	1539
$(2.0)^{***}$	97.1+	468+	0.601	0.70772	0.70770	+ 8.2	1.3	2066
(3.5)***	90.8+	383+	0.687	0.70962	0.70959	+ 9.1	1.7	1376
—	168	300	1.62			+ 7.8	9.8	681
_	107	390	0.79			—	2.3	328
— .	168	290	1.68			—	2.4	1534
4.5 ± 0.7 (w. r.)	112+	395+	0.82	0.70998	0.70993	+10.4	1.9	1562
(3.5)***	162+	315+	1.49	0.71067	0.71060	+ 8.7	2.7	840
	174	290	1.74			—	2.7	1069
(3.5)***	127+	308+	1.19	0.71071	0.71065	+10.7	2.4	1553
_	157	290	1.57		—		3.0	1018
	154	280	1.59	—		_	2.6	1081
	129	380	0.98			_	2.0	1564
	114	360	0.92			_	2.3	624

Geochemical Studies of Upper Cenozoic Igneous Rocks (Gardeweg et al.)

Cenozoic igneous rocks of Guatiquina area, Antofagasta, Chile.

+ Determined in the GSJ, the rest of the analyses were done in the Servicio Nacional de Geología y Minería, Chile.

-555-

rocks in Japan (ISHIHARA, 1979a). That is, the Chilean rocks occupy the lower half of the magnetite-series field in magnetic susceptibility vs. SiO_2 plot (Fig. 4).

Subvolcanic rocks which are the oldest in the studied areas are divided into three groups in their magnetic susceptibility. The oldest, 13 Ma group in the Poquis area has an intermediate value of $589-732 \times 10^{-5}$ SI. The next group of 8 Ma in the Cordones Quilapana and Ceja Alta areas has the highest values as $1115-1417 \times 10^{-5}$ SI. The youngest 5 Ma group at Arenoso and Chivato Muerto has the lowest values as $37-135 \times 10^{-5}$ SI.

The highest group (GMC-3, 10, 11 and 12) contains many polygonal magnetites as phenocryst and also fine crystals in the groundmass. But color of the biotite is Z = Y =reddish brown. The intermediate one contains lesser amount of phenocrystic magnetite which is primary and also secondary magnetite which formed after decomposition of biotite by alteration (GMC-7) or only fine crystals of magnetite in the groundmass (GMC-121). The lowest group (GMC-20, 21 and 23) also contains phenocrystic magnetite but has corroded outline. This magnetite is converted to hematite by alteration to lower the magnetic susceptibility. The biotite of Z = Y color is abnormally reddish brown which may be partly due to limonite staining.

The subvolcanic rocks contain generally magnetite and the variety of the magnetic susceptibility is resulted from the original low content of magnetite (Poquis rocks) and hematitization over magnetite by hydrothermal alterations (Arenoso and Chivato Muerto).

Among stratovolcano-related rocks, the El Laco andesite has the highest value (2066 × 10^{-5} SI). This contains many phenocrysts of polygonal and some cubic magnetite. Most of the others are also high in the range of $840-1,600 \times 10^{-5}$ SI. These rocks contain magnetite as phenocryst and fine crystals in the groundmass. A few of the low values ($624-681 \times 10^{-5}$ SI) are obtained on andesite having little magnetite (PG-214) or on rocks whose matrix is glassy (PG-212, 234), indicating some of the groundmass magnetite formed during the devitrification.

Lithic welded tuffs interbedded with the andesites have high magnetic susceptibility (1069, 1534×10^{-5} SI). These rocks contain abundant phenocrysts of magnetite and the biotite color is greenish brown; thus showing truely magnetite-series character.

Among lava dome felsic rocks, fresh one (GMC-1, 1261×10^{-5} SI) has high magnetic susceptibility and contains phenocrystic magnetite. But low ones (GMC-6, 6-1, 225-245 $\times 10^{-5}$ SI) contain only few magnetite phenocrysts and the groundmass is glassy.

Welded tuffs are highly magnetic as 950– 1409 \times 10⁻⁵ SI. The rocks contain many phenocrystic magnetite and Z=Y color of the biotite is greenish brown to brown and some (GMC-5, 19) have reddish brown color.

Most of the studied rocks have magnetite as phenocryst, so that they may be called magnetite-series rocks. However, their magnetite contents are less than those of typical magnetite-series rocks and Z = Y color of the biotite is often reddish brown. Thus, they have an intermediate character between typical magnetite-series and ilmenite-series rocks. Although further detailed studies need to be done, some of the studied rocks may possibly belong to ilmenite series. They are quartz porphyries at Poquis (GMC-7, 121), andesites at Morado Hill and glassy rhyolite dome at Jarellon Hill (GMC-6, 6-1); all located at north of latitude 23°00/S.

Tin Contents

Trace amount of tin in igneous rocks and its relation to Sn mineralization are very well established in granitic terrains (ISHIHARA and TERASHIMA, 1977). Even in volcanic areas where the Kuroko type deposits occur, Snrich volcanic rocks are observed related to cassiterite-bearing massive sulfide deposits in the Canadian shield, whilst tin is very poor in volcanic rocks around the Sn-free Kuroko



Fig. 5 Tin vs. SiO_2 content of the studied volcanic rocks. The areas for the Japanese and Canadian volcanic rocks are taken from ISHIHARA and TERASHIMA (1982, 1983). Symbols are the same as those of Fig. 4.

deposits in Japan (ISHIHARA and TERASHIMA, 1983).

In the studied areas, tin contents are generally as low as 1.1–3.7 ppm (Table 1). This range is similar but slightly higher than that of volcanic rocks related to the Kuroko mineralization in Japan (Fig. 5). Among the studied rocks, the Huailitas andesites are somewhat enriched in tin as andesite, giving rise to an average of 3.2 ppm (n=9), because of particularly high value of 9.8 ppm on a glassy andesite (PG-212). If this rock is excluded, the average is 2.3 ppm (n=8). The Jachi andesites are especially low in Sn (average 1.5 ppm). Among other volcanic rocks, rhyolite dome of the Jarellon Hill gives high values as 3.4 and 3.7 ppm, which could well be an ilmenite series.

All the subvolcanic porphyries are depleted in tin as 1.3-2.0 ppm. The values are much lower than those of porphyries in the Bolivian tin belt of 2.7 to 21.0 ppm Sn (average 8.5 ppm, n=5, ISHIHARA and TERASHIMA, unpublished data). The cassiterite-mineralized porphyries at Poquis are not particularly enriched in tin. However, these analyses may not represent the original values because of the hydrothermal alteration observed on these porphyries. In the Akenobe subvolcanic tin lodes area in southwestern Japan, two contrasting values are seen on fresh rocks (avg. 6.0 ppm) and altered rocks (avg. 1.7 ppm, TERASHIMA and ISHIHARA, 1982), and the tin is considered to have been leached out through the hydrothermal alteration due to meteoric water circulation during a deuteric stage.

The general paucity of tin in the Chilean rocks indicates that Sn-rich igneous bodies equivalent to "tin granite" do not widely exist in the studied area. It follows that Sn-rich continental crust which would have been a source for the Bolivian Sn-carrying igneous rocks does not continue to the south, into the northern Chile.

Oxygen and Strontium Isotopic Characteristics

Oxygen isotopic ratios (¹⁸O/¹⁶O) were determined for 14 samples including 6 sub-volcanic rocks and related ignimbrite, and 8



Bulletin of the Geological Survey of Japan, Vol. 35, No. 11

Fig. 6. δ^{18} O vs. SiO₂ content of the studied rocks. Letters with the data points for lavas indicate the stratovolcanoes from which the lavas came out: J, Jachi volcano; L, Laco volcano; and H, Huailitas volcano. Data for altered rocks are indicated by asterisk. The compositional ranges of Quaternary volcanic rocks, and ilmenite-series and magnetite-series granitoids of Japan were taken from MATSUHISA (1979) and MATSUHISA *et al.* (1982).

volcanic rocks. The analytical method is described in MATSUHISA (1979). The data are presented in terms of δ -notation relative to SMOW. A plagioclase sample separated from GMC-12 dacite porphyry was analyzed together with several whole-rock samples of altered subvolcanic rocks (GMC-10, 12 and 23), aiming at detecting hydrothermal activity after crystallization.

 87 Sr/ 86 Sr ratios were determined for 10 fresh whole-rock samples for which oxygen isotopic data were available. The analytical method is the same as described in SHIBATA *et al.* (this volume). The present ratios were corrected to the initial values by applying the observed or assumed K–Ar ages of the rocks. Fresh whole-rock samples would provide isotopic compositions of their magmas and subsequently constraint on their source material.

The δ^{18} O values are plotted against wt percent SiO₂ of the rocks in Fig. 6. The composition ranges of Quaternary volcanic rocks and the magnetite- and ilmenite-series granitoids from Japan (MATSUHISA, 1979; MATSUHISA *et al.*, 1982) are shown for comparison. It is obvious that the rocks from the Guatiquina area, except for a glassy rock (PG-212) and an altered subvolcanic rock (GMC-10), are distributed in the composition range of the ilmenite series granitoids, having δ^{18} O values of +8 to +11 per mil. These values are comparable to those of andesites from northern Chile and northwestern Argentina reported by HARMON *et al.* (1981), but higher than those for Ecuador (HARMON *et al.*, 1981) and central and southern Chile (LONGSTAFFE *et al.*, 1983; MUEHLENBACHS and STERN, 1980). The high δ^{18} O values suggest involvement of ¹⁸O-rich crustal material in the andesitic magmatism.

The δ^{18} O values of the altered subvolcanic rocks GMC-10, 12 and 23 range from +7.8 to +10.2 per mil. Among those, GMC-10 and 12 are from a subvolcanic complex, Cordon de Ceja Alta. There is no distinct correlation between isotopic composition and apparent degree of alteration. However, plagioclase of GMC-12 has a δ^{18} O value of +7.5 per mil, being 1 per mil lower than the whole-rock value. Since plagioclase is the mineral which reacts most readily with thermal waters in respect of oxygen isotopes, its ¹⁸O-depletion suggests hydrothermal activity with low-¹⁸O waters (consequently of meteoric origin) after crystallization. It is supposed that potential mineralization might exist relating to this subvolcanic complex.

The initial 87 Sr/ 86 Sr ratios range from 0.7069 to 0.7131, and show a negative cor-



Fig. 7 (⁸⁷Sr/⁸⁶Sr)₀ vs. ppm Sr of the studied rocks. Symbols are the same as in Fig. 6.

relation with Sr concentration (Fig. 7). Since magmatic processes do not produce any significant isotopic fractionation of strontium, these results suggest contamination or assimilation of Sr-isotopically different material to the magmas. This relationship is interpreted by either mixing of a mantle-derived component of low ⁸⁷Sr/⁸⁶Sr and high Sr with a crustal component of higher ⁸⁷Sr/⁸⁶Sr and lower Sr (FRANCIS *et al.*, 1980), or combined processes of wall-rock assimilation and fractional crystallization (BRIQUEU and LANCELOT, 1979; DEPAOLO, 1981).

HARMON et al. (1981) discussed combined assimilation-fractional crystallization models for the Andean lavas on the $\delta^{18}O^{-87}Sr/^{86}Sr$ diagram, in which end-member compositions were taken as $\delta^{18}O = 5.7$, ${}^{87}Sr/{}^{86}Sr = 0.703$ for hypothetical mantle and $\delta^{18}O = 19$, ${}^{87}Sr/$ 86 Sr = 0.735 for isotopically evolved crust. In their models the ratio of Sr concentration in the end-members (mantle: crust) was assumed to be 5:1. The present results also show a positive relationship between δ^{18} O and 87 Sr/ ⁸⁶Sr (Fig. 8). Therefore, roughly speaking, they accord with the mixing model of low- δ^{18} O, $-^{87}$ Sr/ 86 Sr mantle-derived material with high-818O, -87Sr/86Sr crustal material. However, the slightly convex downward curvature



Fig. 8 δ^{18} O vs. (87 Sr/ 86 Sr)₀ of the studied rocks. Symbols are the same as in Fig. 6.

--- 559 ---



Fig. 9 Plots of $\delta^{18}O(a)$ and $({}^{87}Sr/{}^{86}Sr)_0(b) \nu s$. latitude south of sample locations. Data for altered rocks are not included. Symbols are the same as in Fig. 6.

of the postulated mixing line suggests that the Sr-concentration of the crustal end-member would be comparable to or slightly higher than that of magma. This means that the containinating material would be igneous rocks of the older crust. The negative correlation between Sr concentration and ⁸⁷Sr/⁸⁶Sr ratio would be interpreted by combined processes of assimilation and fractional crystallization in this case (DEPAOLO, 1981).

General tendency of increase in δ^{18} O and 87 Sr/ 86 Sr toward north is observed in the studied area except for glassy rocks (Fig. 9a, b). Glassy rocks may not maintain their primary isotopic compositions because of their less resistance to deuteric processes. The δ^{18} O values remain virtually constant at about +8 per mil in the area of 24° to 23°30′S, then sharply increase to +11 per mil at around 23°S. The increase in 87 Sr/ 86 Sr is

rather gradual, reaching the highest values of 0.710 to 0.713 at around 23°S. The high increase in ⁸⁷Sr/⁸⁶Sr at 23°S is strengthened by a quartz porphyry from Poquis (GMC-7). This trend accords with the overall variation of the 87Sr/86Sr ratios of the Quaternary calcalkaline rocks along the Andean belt: the highest values in the border area of Peru, Bolivia, Chile and Argentina, decreasing towards north and south along the Andes (KLERKX et al., 1977; MCNUTT et al., 1975; JAMES et al., 1976; FRANCIS et al., 1977; HAWKESWORTH et al., 1979; THORPE et al., 1979; FRANCIS et al., 1980; HAWKESWORTH et al., 1982). The variation of isotopic compositions of the volcanic rocks may reflect thickness of the crust along the Andes, which acts as the contaminant to the magmas.

HAWKESWORTH *et al.* (1982) reported high ⁸⁷Sr/⁸⁶Sr ratios of 0.7069 to 0.7095 for the volcanic rocks from the Cerro Purico area, which is located west of Cerro Huailitas analyzed in the present study (Fig. 1). It is noticed that these volcanoes are aligned in east-west direction, crossing the general trend of the Andean volcanism. A transverse fault system crossing the subduction zone may exist along this line, and provide conditions favorable for melting of ¹⁸O- and ⁸⁷Sr-rich crustal material.

Summary and Conclusion

The Upper Cenozoic igneous rocks in the Guatiquina area, Altiplano of Antofagasta, northern Chile, are divided into three main rock types: (1) ignimbrites as very extensive sheets, (2) lavas associated with stratovolcanoes and (3) small eruptive centers and subvolcanic porphyries. They are mainly andesities and dacites of calc-alkaline series with a minor amount of shoshonitic association in the easternmost part of the area.

The ignimbrites are dated at 4.1 to 4.8 Ma by the K-Ar method. The lavas of the stratovolcanoes are also dated at similar ages, although the number of age-determinations is very limited. The ages of the subvolcanic rocks are comparatively variable, ranging from the youngest of 4.8 Ma to the oldest of 12.9 Ma determined by the K-Ar method.

Magnetic susceptibility of the studied rocks are mostly between 600 and $1,600 \times 10^{-5}$ SI. This range corresponds to the lower half of the magnetite-series field in the magnetic susceptibility vs. SiO₂ plot given by ISHIHARA (1979a, b). Among stratovolcano-related rocks, an El Laco andesite, which contains many phenocrysts of polygonal and some cubic magnetite, has the highest value of 2066×10^{-5} SI. Some of quartz porphyries, andesites and glassy rhyolites from the area north of latitude 23°S may possibly belong to the ilmenite series.

The Sn contents of the studied rocks are generally as low as 1.1 to 3.7 ppm. Sn-rich igneous rocks equivalent to "tin-granite" do not widely exist in the studied area. Therefore, southwestern prolongation of the Bolivian tin belt to this area does not seem plausible.

The δ^{18} O values and initial 87 Sr/ 86 Sr ratios of the rocks range from +7.8 to +11.2 per mil and 0.7069 to 0.7131, respectively. These results suggest involvement of ¹⁸O- and ⁸⁷Srrich crustal material in the andesitic magmas. General tendency of increase in $\delta^{18}O$ and ⁸⁷Sr/⁸⁶Sr toward north is observed in the studied area with the highest values at around 23°S. This accords with the fact that the ilmenite-series affinity of the rocks is observed in the same area. Contribution of crustal material to the andesitic magmas would be large in the area around 23°S. This may be attributed mainly to the crustal thickness under the area, and partly be due to a possible transverse fault system crossing the subduction zone.

References

ALLMENDINGER, R. W., RAMOS, V. A., JORDAN, T. G., PALMA, M. and ISACKS, B. L. (1983) Paleogeography and Andean structural geometry, Northwest Argentina. *Tectonics*, vol. 2, p. 1–16.

BRIQUEU, L. and LANCELOT, J. R. (1979) Rb-Sr

systematics and crustal contamination models for calc-alkaline igneous rocks. *Earth Planet. Sci. Lett.*, vol. 43, p. 385–396.

- COIRA, B., DAVIDSON, J., MPODOZIS, C. and RAMOS, V. (1982) Tectonic and magmatic evolution of the Andes of Northern Argentina and Chile. *Earth Sci. Rev.*, vol. 18, p. 303– 332.
- DEPAOLO, D. J. (1981) Trace element and isotopic effects of combined wallrock assimilation and fractional crystallization. *Earth Planet. Sci. Lett.*, vol. 53, p. 189-202.
- DERUELLE, B. (1978) Calc-alkaline and shoshonitic lavas from five Andean volcanoes (between latitudes 21°45′ and 24°30′S) and the distribution of the Plio-Quaternary volcanism of the south-central and southern Andes. Jour. Volc. Geotherm. Res., vol. 3, p. 281–298.
- FRANCIS, P. W., MOORBATH, S. and THORPE, R. S. (1977) Strontium isotope data for Recent andesites in Ecuador and north Chile. *Earth Planet. Sci. Lett.*, vol. 37, p. 197–202.
- ——, THORPE, R. S. MOORBATH, S., KRETZ-SCHMAR, G. A. HAMMILL, M. (1980) Strontium isotope evidence for crustal contamination of calc-alkaline volcanic rocks from Cerro Galan, northwest Argentina. *Earth Planet. Sci. Lett.*, vol. 48, p. 257–267.
- GARCIA, F., PÉREZ, E. y CEBALLOS, E. (1962) El Ordovícico de Aguada de la Perdiz. Santiago, Chile. *Rev. Minerales*, vol. 77, p. 52– 61.
- GARDEWEG, M. y RAMIREZ, C. F. (in press) Hoja Rio Zapaleri Región de Antofagasta. Servicio Nacional de Geología y Minería, Carta Geológica de Chile.
- GRANT, J. N., HALLS, C., AVILA, W. and AVILA, G. (1976) Igneous geology and the evolution of hydrothermal systems in some sub-volcanic tin deposits of Bolivia. *Volcanic Processes in Ore Genesis*. Special publication, no. 7, Geol. Soc. London, p. 117–126.
- HARMON, R. S., THORPE, R. S. and FRANCIS, P. W. (1981) Petrogenesis of Andean andesites from combined O-Sr isotope relationship. *Nature*, vol. 290, p. 396-399.
- HAWKESWORTH, C. J., NORRY, M. J., RODDICK, J. C., BAKER, P. E., FRANCIS, P. W. and THORPE, R. S. (1979) ¹⁴³Nd/¹⁴⁴Nd, ⁸⁷Sr/⁸⁶Sr, and incompatible element variations in calcalkaline andesites and plateau lavas from

-561 -

South America. Earth Planet. Sci. Lett., vol. 42, p. 45–57.

- HAWKESWORTH, C. J., HAMMILL, M., GLEDHILL, A.
 R., VAN CALSTEREN, P. and ROGERS, G. (1982) Isotope and trace element evidence for late-stage intra-crustal melting in the High Andes. *Earth Planet. Sci. Lett.*, vol. 58, p. 240–254.
- ISHIHARA, S. (1979a) Kappameter KT-3 and its application for some volcanic rocks in Japan. Bull. Geol. Surv. Japan, vol. 30, p. 513-519.
- (1979b) Lateral variation of magnetic susceptibility of the Japanese granitoids. *Jour. Geol. Soc. Japan*, vol. 85, p. 509–523.
- and TERASHIMA, S. (1977) The tin content of the Japanese granitoids and its geological significance on the Cretaceous magmatism. *Jour. Geol. Soc. Japan*, vol. 83, p. 657–664.
- and (1983) Genesis of tin mineralization in kuroko mineralized belts: Japan and Canada. *Mining Geol. Spec. Issue*, no. 11, p. 103–110.
- JAMES, D. E., BROOKS, C. and CUYUBAMBA, A. (1976) Andean Cenozoic volcanism: Magma genesis in the light of strontium isotopic composition and trace element geochemistry. Bull. Geol. Soc. Am., vol. 87, p. 592–600.
- KLERKX, J., DEUTSCH, S., PICHLER, H. and ZEIL, W. (1977) Strontium isotopic composition and trace element data bearing on the origin of Cenozoic volcanic rocks of the central and southern Andes. J. Volc. Geotherm. Res., vol. 2, p. 49–71.
- LAHSEN, A. (1982) Upper Cenozoic volcanism and tectonism in the Andes of northern Chile. *Earth Sci. Reviews*, vol. 18, p. 285–302.
- LONGSTAFFE, F. J., CLARK, A. H., MCNUTT, R. H. and ZENTILLI, M. (1983) Oxygen isotopic compositions of Central Andean plutonic and volcanic rocks, latitudes 26°-29° south. *Earth Planet. Sci. Lett.*, vol. 64, p. 9-18.
- MCNUTT, R. H., CROCKET, J. H., CLARK, A. H., CAELLES, J. C., FARRAR, E., HAYNES, S. J. and ZENTILLI, M. (1975) Initial ⁸⁷Sr/⁸⁶Sr ratios of plutonic and volcanic rocks of the Central Andes between latitudes 26° and

29° south. Earth Planet. Sci. Lett., vol. 27, p. 305–313.

- MARINOVIĆ, N. (1979) Geologia de los Cuadrángulos Zapaleri y Nevados de Poquis, II Región, Antofagasta. *Memoria para optar al título de geólogo*, Depto. de Geol., U. de Chile.
- MATSUHISA, Y. (1979) Oxygen isotopic compositions of volcanic rocks from the East Japan island arcs and their bearing on petrogenesis. *Jour. Volc. Geotherm. Res.*, vol. 5, p. 271–296.
- ———, SASAKI, A., SHIBATA, K. and ISHIHARA, S. (1982) Source diversity of the Japanese granitoids: An O, S. and Sr isotopic approach. Abstracts 5th International Conf. Geochron. Cosmochron. Isotope Geol., Nikko, Japan, p. 239–240.
- MUEHLENBACHS, K. and STERN, C. R. (1980) δ^{18} O variation among calc-alkaline volcanic rocks from S. Chile: Implications for the effects of ridge subduction on the source region of orogenic volcanism. *EOS*, vol. 61, p. 401.
- MUNIZAGA, F. and MARINOVIĆ, N. (1979) Evidencias preliminares de un volcanismo shoshonitico Cenozoico superior en el área del volcán Zapaleri, A. Región Chile. Actas Congr. Geol. Chilero, Arica-Chile no. 3, E237–E255.
- PACCI, D., MUNIZAGA, F., HERVÉ, F., KAWASHITA, K. and CORDANI, V. (1980) Acerca de la edad Rb/Sr precámbrica de rocas de la Formación Esquistos de Belén, Departamento de Parinacota, Chile. *Rev. Geol. Chile*, vol. 11, p. 43–50.
- RAMIREZ, C. F. y GARDEWEG, M. (1982) Hoja Toconao, Región de Antofagasta. Servicio Nacional de Geología y Minería. Carta Geológica de Chile. n° 54, 121p.
- SHIBATA, K., ISHIHARA, S. and ULRIKSEN, C. E. (1984) Rb-Sr ages and initial ⁸⁷Sr/⁸⁶Sr ratios of late Paleozoic granitic rocks from northern Chile. *Bull. Geol. Surv. Japan*, vol. 35, p. 537–545.
- SILLITOE, R. H. (1972) Relation of metal provinces in western America to subduction of oceanic lithosphere. Bull. Geol. Soc.

Geochemical Studies of Upper Cenozoic Igneous Rocks (Gardeweg et al.)

Am., vol. 83, p. 813-817.

— (1974) Tectonic segmentation of the Andes: implications for magmatism and metallogeny. *Nature*, vol. 250, p. 542–545.

- SWIFT, S. A. and CARR, M. J. (1974) The segmented nature of the Chilean Seismic Zone. *Phys. Earth Planet. Int.*, vol. 9, p. 183–191.
- TERASHIMA, S. and ISHIHARA, S. (1982) Tin Abundance in the Cretaceous granitoids around the Akenobe mine area, Japan. *Mining*

Geol., vol. 32, p. 73-76.

- THORPE, R. S., FRANCIS, P. W. and MOORBATH, S. (1979) Rare earth and strontium isotope evidence concerning the petrogenesis of north Chilean ignimbrites. *Earth Planet. Sci. Lett.*, vol. 42, p. 359–367.
- TRAVISANY, V. y Díaz, F. (1978) Estudio geológico económico y geoquímico del sector Nevados de Poquis. *IIG, ined.*

チリ、アントファガスタ・アルティプラノの上部新生代火成岩類の地球化学的研究

M. ガルデヴェク・石原舜三・松久幸敬・柴田 賢・寺島 滋

要 旨

北部チリ,アントファガスタ・アルティプラノのグァティキナ(Guatiquina)地域の上部新生代火成 岩類について,帯磁率, Sn, Rb, Sr 含有量,及び O, Sr 同位体比を測定した. 岩石は,主としてカ ルク・アルカリ岩系の安山岩,デイサイト,イグニンプライト,及びそれらと等価の貫入岩類である. 測定結果に基づき,大陸プレート縁での火成作用における地殻物質の寄与を検討した.

帯磁率は大部分 600-1,600×10⁻⁵SI の範囲で,磁鉄鉱系列の岩石の値の範囲の下半に相当する. 多く の磁鉄鉱斑晶を含む El Laco 安山岩は最も高い 2,066×10⁻⁵SI を示す. 南緯 23°以北の岩石は,恐ら くチタン鉄鉱系列に属する.

Sn 含有量は一般に 1.1-3.7 ppm と低く, "tin-granite" に相当する Sn に富んだ岩石の分布はみられない. そこで, ボリビアのスズ・ベルトのこの地域への延長の可能性は少ない.

岩石の $\delta^{18}O$ 値及び ${}^{87}Sr/{}^{86}Sr$ 初生比は,それぞれ, +7.8~+11.2 パーミル及び 0.7069-0.7131 の範囲である. ${}^{18}O/{}^{16}O$ 比と ${}^{87}Sr/{}^{86}Sr$ 比の間には正の相関がみられ, ${}^{87}Sr/{}^{86}Sr$ 比は Sr 含有量の減少 につれて増大する. これらの結果は, ${}^{18}O$ と ${}^{87}Sr$ に富む地殻物質が安山岩マグマに混入したことを示 唆する. 調査地では北に向って $\delta^{18}O$ 値, ${}^{87}Sr/{}^{86}Sr$ 比が増大する一般的傾向がみられ,南緯 23° 付近で 最大となる. このことは,南緯 23° 以北で岩石がチタン鉄鉱系となることと調和的である. 安山岩マグ マへの地殻物質の寄与はこの地域で最大となるのであろう: 地殻物質の寄与の程度は,地殻の厚さや, マグマが形成される場の地質構造に依存していると考えられる.

(受付:1984年7月12日;受理:1984年8月9日)