Clays and Clay Minerals, Vol. 55, No. 5, 524–533, 2007.

ZEOLITIZATION OF TUFFS AT QUINAMÁVIDA, CENTRAL SOUTHERN CHILE

SOPHÍA BASCUÑAN, URSULA KELM*, VILMA SANHUEZA AND GUILLERMO ALFARO
Instituto de Geología Económica Aplicada, Universidad de Concepción, Casilla 160-C, Concepción, Chile

Abstract—Tuffs of the Tertiary Colbún Formation near Quinamávida in central southern Chile have been mapped and their mineralogy analyzed. The pyroclastic rocks present a maximum outcropping thickness of 120 m and are dominated by vitreous lapilli and minor lithic tuffs, the products of active volcanism nearby. About 10% of the tuffs consist of lenses of fine banded tuffs with a high leaf content that were deposited in shallow lakes during quiescent periods between periods of volcanic activity. This tuff sequence is pervasively transformed to clinoptilolite/heulandite and mordenite with variable amounts of plagioclase, minor quartz and smectite. Factors thought to have influenced this conversion to zeolites are a humid climate following deposition combined with a slightly elevated heat flow. Local hydrogeological conditions have modified the cation-hydrogen ion ratios across the study area favoring the formation of clinoptilolite/heulandite and mordenite with medium-minor smectite in the center and south, and a more abundant presence of smectite in the north of the study area.

Key Words—Chile, Heulandite, Clinoptilolite, Mordenite, Tuff, Zeolite.

INTRODUCTION

In Chile, little public or scientific attention has been paid to the country's zeolite resources. This is in contrast to copper, Chile's principal commodity, to which considerable research and development efforts have been dedicated in terms of exploration and development of improved production and processing technologies. Official 10-year mineral production statistics (Cochilco, 2004) indicate a modest production of 839 tons of zeolites in 2002, although some extracted zeolite raw materials may be registered in other categories, such as cement additives.

Still, zeolites have been the object of long-standing research in the field of low-temperature metamorphic petrology (*e.g.* Aguirre *et al.*, 2000; Vergara *et al.*, 1993, Levi, 1969), where the Cenozoic volcanic and volcanoclastic sequences at the latitude of Santiago provide a textbook example of zeolite facies in extensional basin settings (Robinson and Frey, 1999).

With respect to high-grade zeolite ore, published data are scarce and often of historic value ('araucanita' by Vila, 1953). In Chile, massive zeolitization of Tertiary tuffs has been observed in the Andean Precordillera of the VII and VIII administrative regions (Figure 1), near the Catillo hot springs (Vila, 1953; Accefo Ltda, 1991; Cabrera *et al.*, 2004). In northern Chile, the III administrative region hosts a vaguely described zeolite deposit (Gajardo, 2000). In addition, zeolitization of rhyolitic and dacitic tuffs was described by Marfil *et al.* (1992) in the II administrative region, near Antofagasta. Some of these zeolite deposits are discontinuously exploited for use as an animal feed additive, for mineral-processing water treatment, as an additive to puzolanic cement, and in the production of ornamental handicraft; the last two uses apply to the Quinamávida deposit.

The objective of this paper is to provide details on the geology and mineralogy of the Quinamávida zeolite deposit (Figure 1) as well as offering some limited initial genetic considerations. It is also hoped that the description of this easily accessible deposit will be the starting point of a more systematic mineralogical examination of Chilean tuffs, many of which have received only mineralogical attention when associated with metallic mineralization. On a less academic level, this study also intends to provide the artisans working the Quinamávida tuffs with mineralogical information that will allow them to promote a wider use of the rock. At the time of writing, a growing number of regional 'zeo-enthusiasts' apply crushed tuff as a soil additive in horticulture.

METHODOLOGY

The area to the east of the village and hot springs of Quinamávida (35º46′–35º50′ S, 71º25′30″–71º28′15″ W) was mapped at a scale of 1:25,000 and sampled based on four general cross-sections and 14 detailed sections vertical to the strike. Sampling was carried out to represent all the lithotypes and color shades present in the tuffs as well as to cover the study region systematically (~200 samples). Once samples had been examined macroscopically, 50 samples were selected for X-ray diffraction (XRD) aided by optical microscopy for textural observations using the same criteria as applied in the field. The clay size fraction (<2 μm) was separated

* E-mail address of corresponding author:
ukelm@udec.cl
DOI: 10.1346/CCMN.2007.0550507

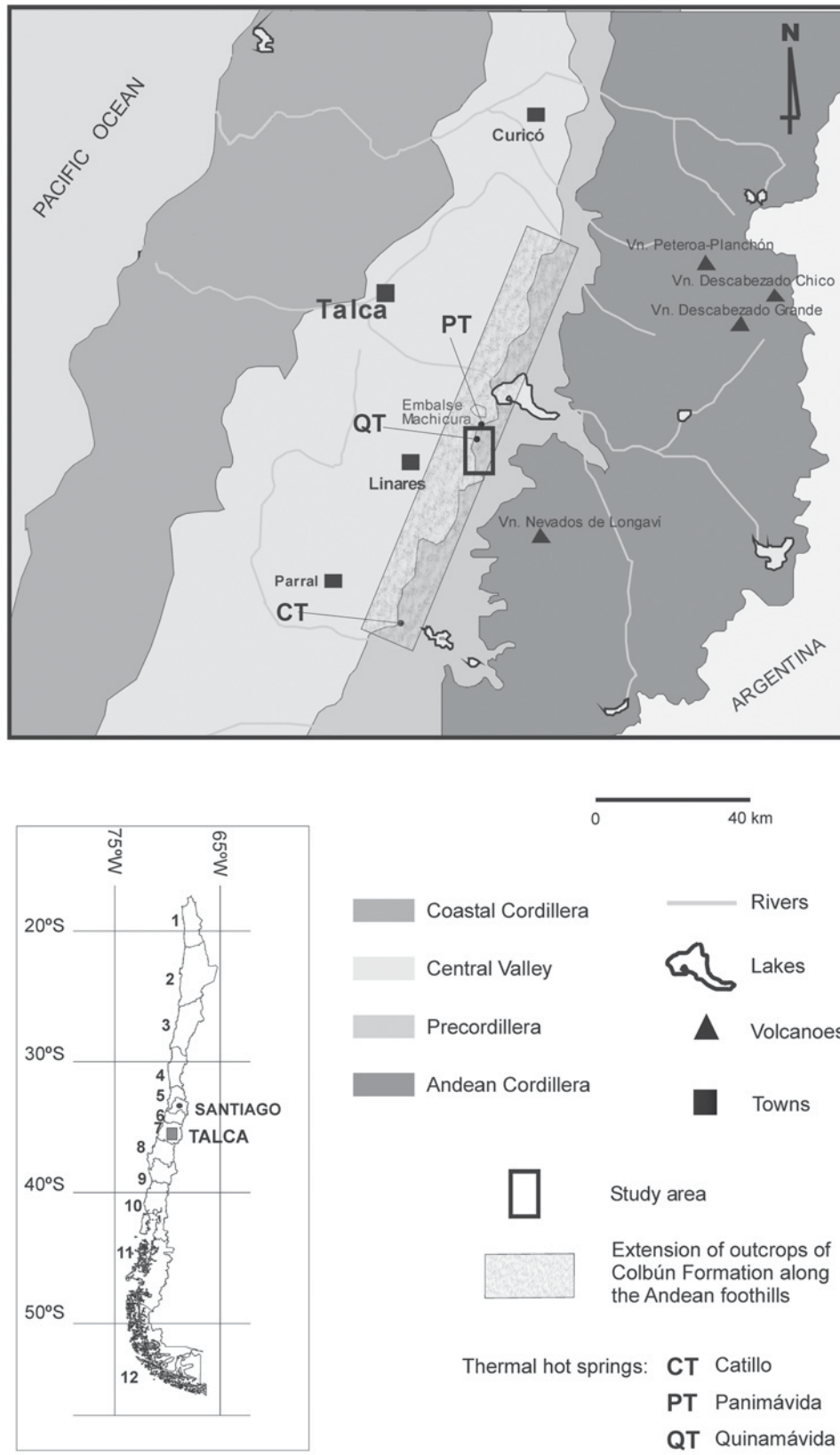

Figure 1. Location of the study area

by centrifugation from ultrasonically disaggregated rock chips. Oriented sample mounts were analyzed in air-dried and ethylene glycol-solvated (70ºC for 24 h) conditions, and heated to 375ºC following the procedures outlined by Moore and Reynolds (1997). A Rigaku Dmax-C diffractometer equipped with a horizontal goniometer was used and operated with Ni-filtered Cu radiation. Major element analyses were carried out for 21 samples on a Rigaku 3070E X-ray fluorescence (XRF) spectrometer. For scanning electron microscopy (SEM), an ETEC autoscan device was used.

GEOLOGICAL FRAMEWORK

Central-southern Chile is characterized by four main morphological units (Figure 1): the coastal cordillera, a central valley filled with Quaternary sediments, the Andean foothills and the principal Andean chain. The study area is situated at the border between the central valley and the Andean foothills and is part of the Tertiary Colbún Formation (Karzulovic *et al.*, 1979). It consists of a sequence of lavas, andesitic breccias and intercalations of tuffs, sandstone and shale. The sequence is interpreted as the infill of a rapidly subsiding continental basin with the presence of active volcanism and elevated geothermal gradient (Vergara, 1985) and extends 125 km along the base of the Andean foothills (Figure 1). An early Tertiary to mid Tertiary age was proposed by Karzulovic *et al.* (1979) based on radiometric dating and fossil flora. Vergara *et al.* (1999) modified the suggested age span from late Eocene to mid Miocene based on new K-Ar and Ar-Ar ages and on paleobotanical data.

Its detailed subdivision has been location-bound, but consensus exists on a basal pyroclastic unit, followed by lake sediments (Karzulovic *et al.*, 1979; Vergara, 1985) and an uppermost unit of lavas (Karzulovic *et al.*, 1979; Vergara, 1999). For the purposes of mapping – without aiming to contribute to a stratigraphical discussion – the Colbún Formation at Quinamávida has been divided into two informal units: a volcanoclastic one and a volcanic one. For the volcanoclastic unit composed of tuffs (and the focus of this communication) a pyroclastic sub-unit and a lake sub-unit were distinguished. The volcanic unit is composed of lavas and breccia sub-units.

Regional structures in Mesozoic and Tertiary rocks follow a N20º–E30º strike, also marked by the main morphological units in this part of the country (Figure 1). A fault is inferred for the contact of the Colbún Formation with the central valley sediments.

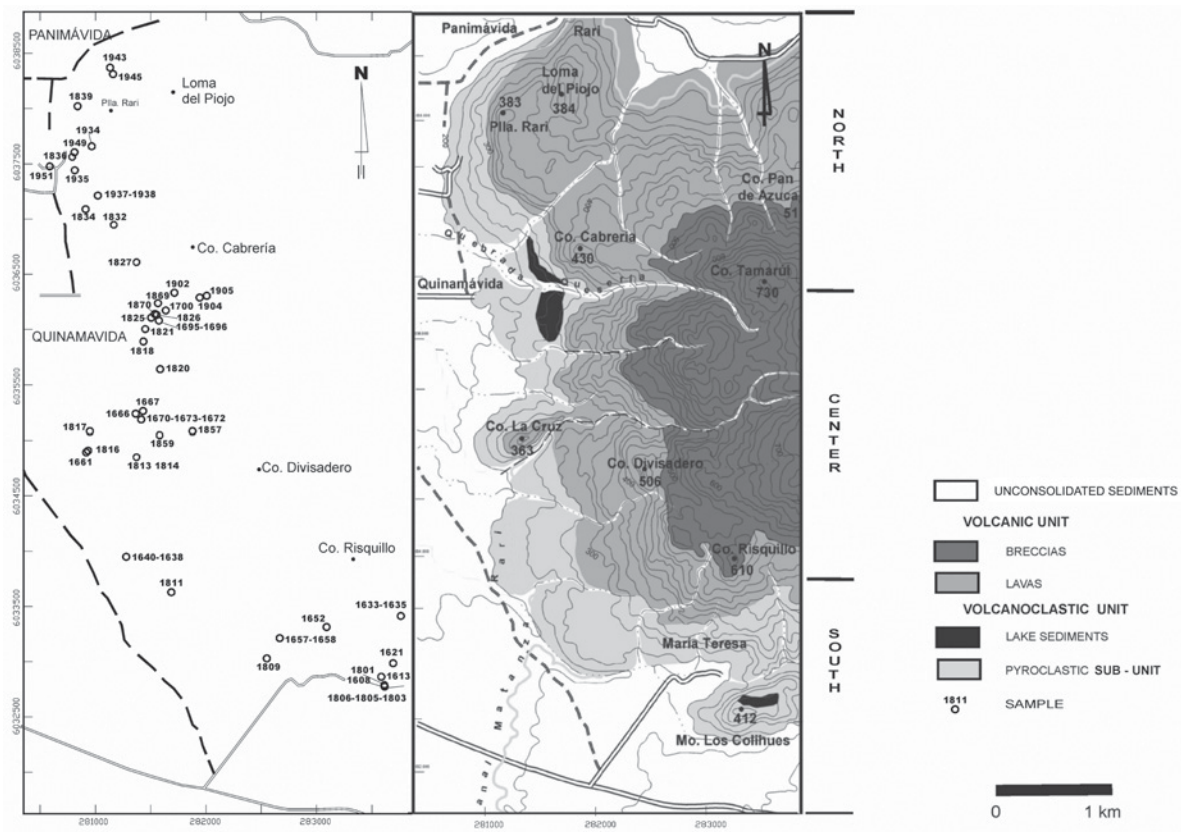

Figure 2. Lithological map of the Colbún Formation tuffs, lavas and breccias at Quinamávida. Sample locations are shown on the map to the left.

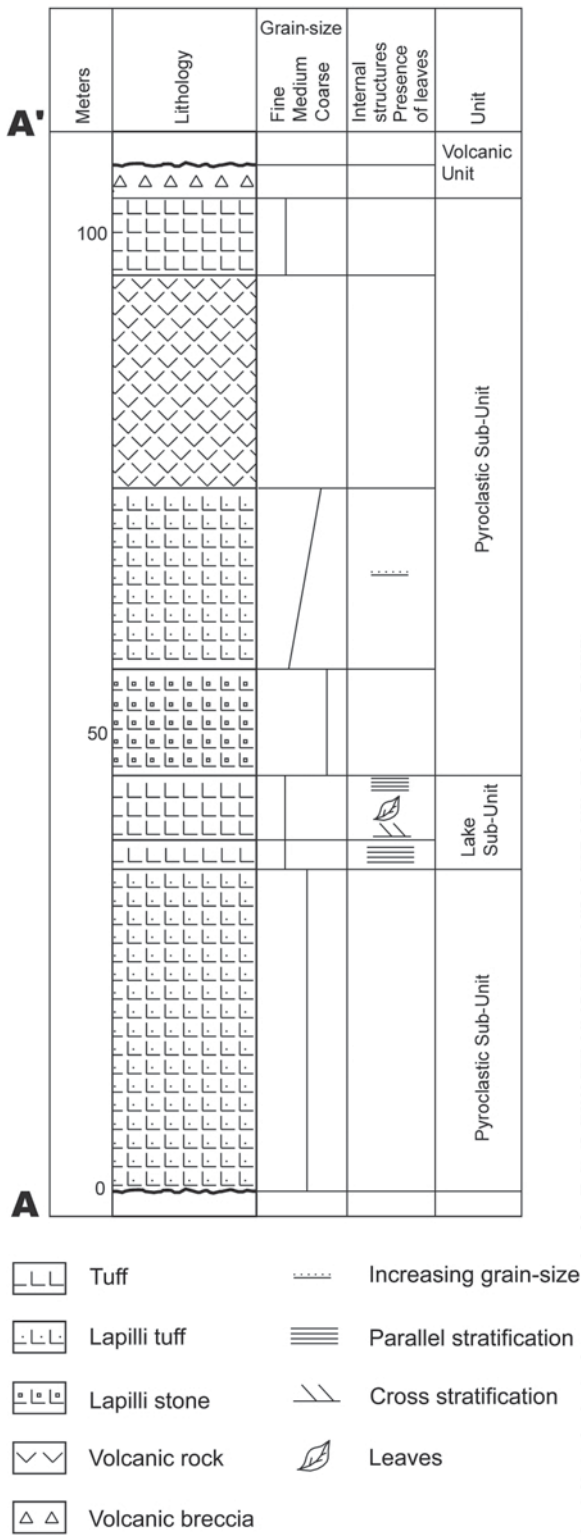

Figure 3. Typical cross-section of the Colbún Formation tuffs; the location of the section is marked in Figure 2.

Less frequent are lineaments of NW–SE to EW orientation (Karzulovic *et al.*, 1979). The contact between the central valley and the Andean foothills is also lined with hot springs, associated with the Chilean southern volcanic zone (Hauser, 1997). Three hot springs are reported close to zeolitic tuffs in Central Southern Chile: Panimávida, Quinamávida and Catillo (Figure 1). Most waters are NaCl- or sulfate-rich; at present, the waters at Quinamávida are reported to be Na_2CO_3-rich, with spring locations moving over short distances during recent decades (Hauser, 1997).

RESULTS AND DISCUSSION

Macroscopic and microscopic information

The pyroclastic sub-unit comprises the basal section of a maximum 120 m vertical thickness (Figures 2, 3), followed uphill by the volcanic unit, which at its base is composed of up to 200 m of lavas followed by breccias up to the hill tops.

The pyroclastic unit is composed of white, beige, buff and pale green colored vitreous tuffs and subordinate lithic tuffs (Schmid, 1981). It contains matrix-supported, badly sorted lapilli, fragments of pumice and lithoclasts (pyroclasts and epiclasts) as well as minor quartz, plagioclase and pyroxene crystals (Figure 4). Under the microscope, the matrix appears to be vitreous (Figure 5). Fossil tree trunks up to 50 cm in diameter are found. Coal reflectance measurements (R 0.20%) carried out on telinite from the south of the study area indicate a sub-bituminous level of coal maturity. These coarse tuffs comprise >90% of the outcrops of the volcanoclastic unit. The remainder are taken up by lenses of finely banded and cross-laminated tuffs and lapilli tuffs with a vitreous matrix. They form cm- to meter-thick sequences with significant leaf content. Due to their 'wood-like' banding and attractive pale green and light brown colors, these tuffs are the most sought after as raw materials for ornamental handicraft, such a rustic bowls, lamp bases,

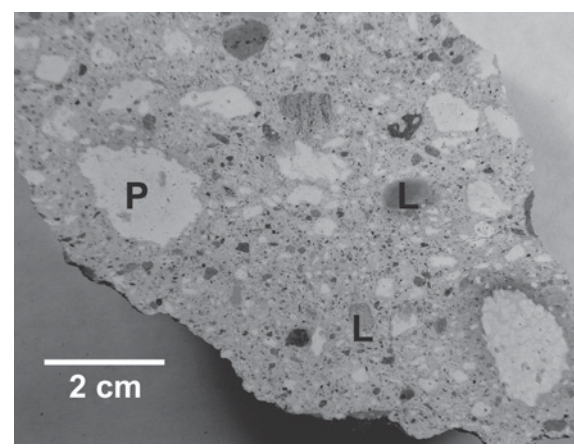

Figure 4. Matrix-supported lapilli-tuff (P – pumice, L – lithic fragment).

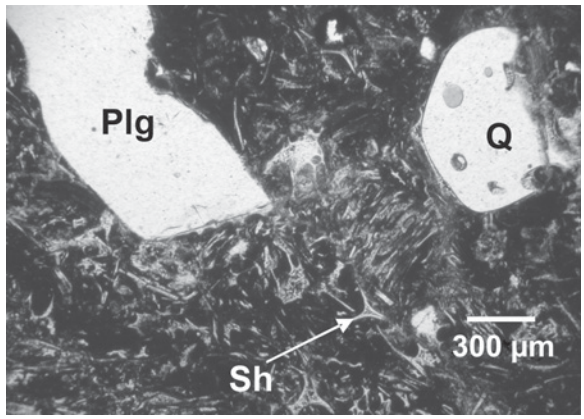

Figure 5. Photomicrograph (under crossed nicols) of a lapilli-tuff (sample 1633) (Plg – plagioclase, Q – quartz, Sh – glass shards).

etc. Two large bodies are marked in Figure 2 and one of them can be observed on the section of Figure 3. Contact with the surrounding coarser-grained pyroclastic rocks is neat and tuffs appear to fill shallow basins.

The overlying volcanic unit is clearly distinguished by its dark color and is composed of porphyric and aphanitic lavas of andesitic and andesitic-basaltic composition and volcanic breccias and pyroclastic rocks of the same composition at its base. This unit covers concordantly the pyroclastic unit. The overlying breccias stand out due to their reddish color (presence of hematite) and the large number of vesicles which are often filled by clinoptilolite and calcite.

Field, macroscopic and microscopic observations suggest that >90% of the pyroclastic unit was deposited during a period of nearby active volcanism, although the precise location of the volcanic complex is unknown. The fine layered tuffs interspersed in coarse pyroclastic deposits are considered to be the product of deposition in shallow lakes or ponds. The ash and minor lapilli could have been blown by the wind, slowly settling on lake bottoms to form a parallel layering or produce a cross stratification at the mouth of small creeks in the case of water transport. The fine grain-size and abundance of organic matter point to a temporal quiescence of the eruptive activity.

The presence of tree trunks, leaves and pollen, particularly abundant in the fine layered tuffs, indicates a continental environment and – apart from narrowing the age span of deposition of this sequence to late Eocene–mid Miocene (Vergara *et al.*, 1999) – the presence of pollen of *Myrtaceidites eugenioides* and *Cyattridites meior* and epiphytic mushrooms indicate a humid climate (S. Palma, pers. comm.).

Zeolitization

Zeolitization was observed in most of the 50 samples analyzed, forming heulandite/clinoptilolite and mordenite (Figure 6). For the 120 m thick, exposed tuff sequence, no vertical differences were observed in the mineralogy by XRD. Accompanying phases are plagioclase, minor quartz and a variable presence of smectite. No opal has been identified. The following variations were observed across the study area: minor quartz is found indistinctly in the coarse pyroclastic sequence as well as in the banded limnic sediments, and plagioclase XRD reflections were found to be more intense in the lapillite and lapilli tuffs of the pyroclastic sequence. Samples with only heulandite/clinoptilolite are more frequent in the north of the study area (Figures 2 and 6, Table 1), whereas the additional presence of mordenite is a regular feature in the center and south. The intensity of the smectite peak in the <2 µm fraction diminishes from north to south. The greatest smectite XRD intensities were observed in samples from creeks and from the lower slopes close to the central valley, with

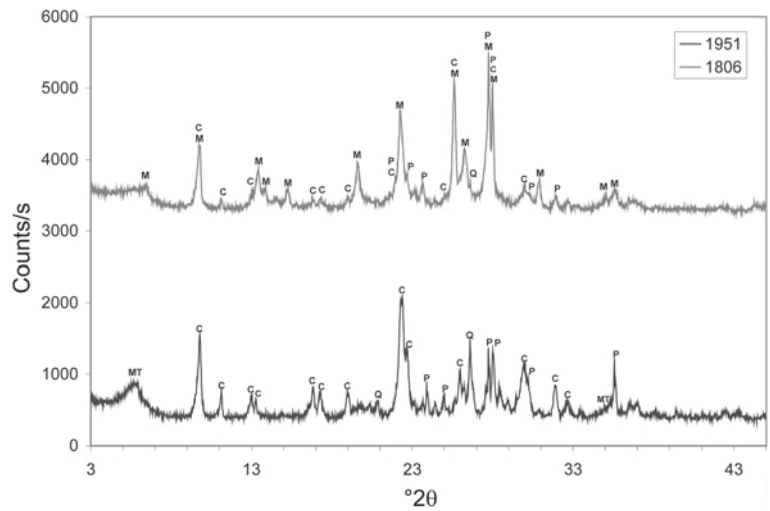

Figure 6. Representative XRD patterns of two tuffs (1951 – north, 1806 – south), MT – montmorillonite (smectite), M – mordenite, C – clinoptilotlite/heulandite, P – plagioclase; Q – quartz. Cu radiation.

Table 1. Summary of whole-rock XRD information and the relative basal intensity of the smectite ethylene glycol reflection in the <2 μm fraction. Samples are listed N−S.

Sample	Clinoptilolite/ heulandite	Mordenite	Quartz	Feldspar	Smectite EG peak intensity in the <2 μm fraction
1943 North	P	Tr		P	High
1839	P		Tr	P	Medium
1949	P		Tr	P	High
1836	P		Tr	m	High
1951	P	Tr	Tr	m	Medium
1937				m	High
1938	P		Tr		High
1834	P	Tr	Tr	P	High
1832	P	m		P	High
1827	P	m	Tr		High
1902		m	Tr	P	High
1905	P		Tr	P	High
1904	P		Tr	P	High
1869	P	P		P	Medium
1700	P		Tr	P	High
1826	P	P	Tr	P	Low
1825		m	Tr		Low
1697		m	Tr		Medium
1695		m	Tr		Low
1696	Tr	m		P	Medium
1821	P	m			Low
1818	P	P	Tr		High
1820		P	Tr	P	Low
1666	P	m	Tr	P	Low
1670	P	m	Tr		Low
1673	P	m	Tr	P	Medium
1857	P		Tr		Medium
1817	P	m		P	Low
1859			P	M	Medium
1816	P	m	Tr		Medium
1661	P	Tr	Tr	m-P	Medium
1813			P	M	High
1814			P	M	Low
1640	Tr		Tr		Low
1638		Tr	Tr	P	High
1811	P		Tr	P	Medium
1672	P	P		P	Low
1634	P	m	Tr		Low
1635	P	m	Tr		Medium
1657	P	m	Tr		Low
1658		m	Tr		Low
1633	P	m	Tr	P	Low
1809	P	m	Tr	P	Medium
1621	P	Tr	Tr	P	Medium
1613	P	Tr	Tr		Medium
1608		M		m	High
1803	P	P	Tr	P	Low
1805	P	m		P	Low
1806	P	P	Tr	P	Low
1801 South		P	Tr	P	Medium

M: major phase; P: phase present; m: minor phase; Tr: phase at trace level

abundant water or moisture (Figure 7). However, denser sampling is required to confirm these observations.

The SEM images reveal tabular-columnar and fan-shaped intergrowths (Figure 8a,b,d) of clinoptilolite/heulandite crystals; smectite presents a typical honeycomb texture (Figure 8a,c). In Figure 8, fibrous mordenite forms on a base of clinoptilolite/heulandite in presence of smectite. The abundance of vitreous shards in microscopic observation (Figure 5) points to the formation of smectite and clinoptilolite/heulandite from

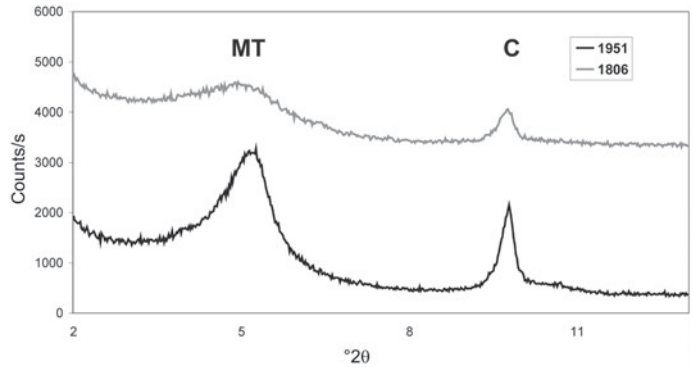

Figure 7. XRD pattern of ethylene glycol-saturated oriented <2 μm size fraction (1951 – north, 1806 – south). Symbols as in Figure 6. Cu radiation.

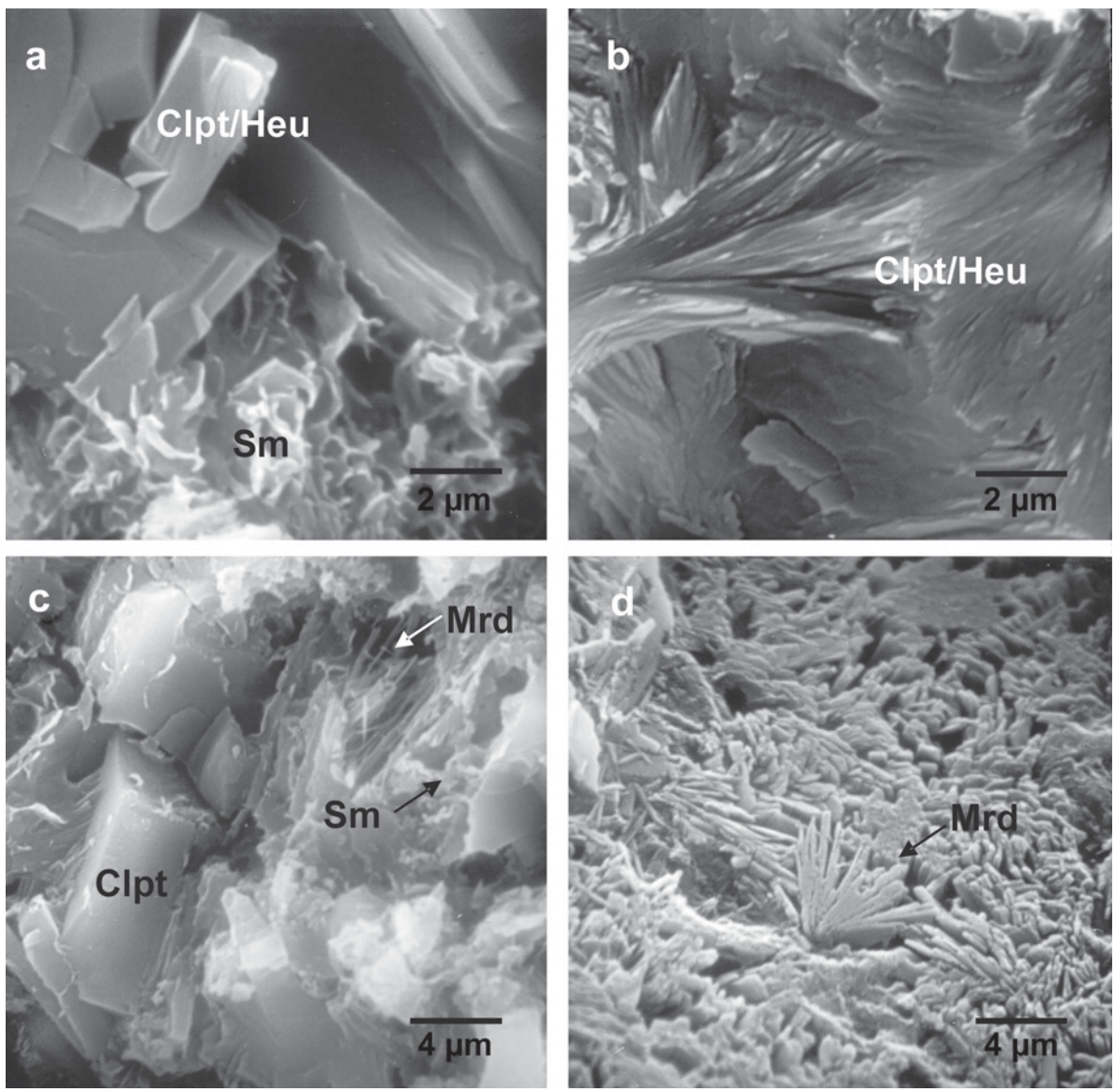

Figure 8. SEM images of samples 1836 (a, b), 1805 (c) and 1870 (d).

vitreous material, without the ability to demonstrate the initial formation of a smectite phase (Chipera and Apps, 2001) in order to raise pH for a subsequent zeolitization.

Major-element whole-rock analyses show a vague N–S variation. Smaller SiO_2 contents and larger amounts of Fe_2O_3 are found in the north (Table 2). Due to mineral size and intergrowth of the zeolite phases (Figure 8) no micro-chemical analyses were obtained. The range of SiO_2/Al_2O_3 ratios for all samples is 4.14 to 7.72 and the $(K_2O+Na_2O)/(CaO+K_2O+Na_2O)$ ratio ranges from 0.24 to 0.41. For samples with clinoptilolite/heulandite and little or no mordenite, the SiO_2/Al_2O_3 ratio spans values from 5.10 to 4.14, whereas with more pronounced presence of mordenite ('P' or 'm' intensity classifications in Table 1) this ratio extends to more silicic whole-rock compositions of 7.72 to 4.96. For the cation ratio of clinoptilolite/heulandite and mordenite samples, a range of 0.30 to 0.46 is observed; the ratio widens for samples with trace levels or no mordenite to 0.24 to 0.48. This compositional shift is in agreement with individual zeolite phase compositions described by Chipera and Apps (2001).

However, based on the N–S lithological continuity of the tuffs, a similar 'starting composition' of the tuffs is assumed. In the north, greater availability of H_2O may have contributed to reduction of the cation/hydrogen ion ratio (Sheppard and Hay, 2001) as well as to the removal of Si from this open-water-flushed system, thus favoring an enhanced formation of smectite instead of zeolite. The absence of opal would support this idea since it would have been easily solubilized (Chipera and Apps, 2001; Christidis, 1998). Some Fe could have been transported from the overlying red hematite-bearing breccia sub-unit, although no crystalline Fe phases have surpassed XRD limits of detection. No analyses from the zeolite-free section of the tuff of the Colbún formation were available to evaluate element depletion or enrichment.

Large-scale zeolitization of silicic non-marine tuffs, *e.g*. at the Quinamávida deposit, has been genetically assigned to open or partly closed hydrological systems (Sheppard and Hay, 2001), although other genetic elements such has hydrothermal activity (Utada, 2001a) or elevated heat flow should not be ruled out.

Mordenite is assigned slightly higher temperatures of formation than clinoptilolite/mordenite in hydrothermal and burial diagenetic/metamorphic environments (Utada, 2001a, 2001b); this observation is also corroborated by synthesis experiments (summarized by Gottardi and Galli, 1985) where greater temperature and increased time of crystallization favored the formation of mordenite in addition to clinoptilolite. As an explanation for the regular presence of mordenite in the center and south an increase in the geothermal gradient would be the most expedient argument.

However, changing hydrological conditions across the study area may have contributed to a N–S temperature variation. Greater access by meteoric water resulting in a more open hydrological regime in the north, as supported by the greater spread of smectite, may also have reduced the temperature of the rock, whereas a more closed system allowed for temperatures to be maintained in the center and south, favoring a more regular crystallization of mordenite. The thermal insulating properties of thick pyroclastic sequences have been described by d'Gennaro *et al.* (2000). The formation of little lagoons (lake sub-unit) intercalated with the pyroclastic sub-unit suggests that the tuffs initially had a restricted permeability (partly closed).

The presence of thermal hot springs has been considered as a motor and cation supplier for zeolitization in deposits in Turkey (Kaçmaz and Köktürk, 2006). In the case of the tuffs of the Colbún formation, hot springs at Catillo and Quinamávida follow the limit between the Central Valley (on valley level, Hauser, 1997) and the Pre-Cordillera (Figure 1). The present-day Quinamávida hot spring is located in the north of the study area and no information or evidence has been found of any such occurrence further south. The extent of its influence on the rocks of the Colbún Formation is difficult to evaluate without the availability of drill holes.

The regional continuity of tuff zeolitization within the Colbún Formation has yet to be studied, but information about the zeolite deposits near Catillo and Quinamávida (Figures 1, 2) point to regional geological conditions favoring this process: (1) an initially humid climate based on paleobotanical data implies a deposition of the tuff in a wet climate; and (2) the vicinity of volcanic centers that increased the geothermal gradient (Vergara, 1985). The presence of hot springs should be considered as evidence of past and present increased heat flow but it is not clear that they are the driving force for this large-scale zeolitization. Given the 'even' zeolitization of the Quinamávida tuffs, and with the limited information at hand, a combination of aspects 1 and 2, both enhancing the reactivity of vitreous material (d'Gennaro *et al.*, 2000) appears the most likely explanation for the driving agent of zeolitization, making this deposit an example of mixed origin without invoking extreme conditions for any of the contributing factors. The sub-bituminous coal maturity detected in the tuffs points to a raised but not extreme geothermal gradient that did not result in the formation of wairakite, for example, which is associated with intense geothermal activity (Chipera and Apps, 2001).

CONCLUSIONS

The zeolitization of the vitreous, lithic and lapilli tuffs and lapilli stone of the Tertiary Colbún Formation at Quinamávida is considered to be due to the combined action of a humid climate at time of deposition of the tuff and a moderately raised regional heat flow. The

Table 2. Major element analyses (wt.%) of 21 samples.

Sample	Observations	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	LOI	Total	SiO_2/Al_2O_3	$(K_2O+Na_2O)/(CaO+K_2O+Na_2O)$
	North														
1943	C/H	58.38	13.45	9.56	0.13	1.60	5.05	2.32	1.22	1.23	0.11	6.56	99.63	4.32	0.41
1945		54.10	12.72	6.99	0.10	2.32	6.88	0.51	1.91	0.85	0.09	14.48	100.95	4.43	0.26
1834	C/H	57.89	13.98	6.79	0.09	2.26	5.22	0.70	0.57	0.91	0.07	12.00	100.48	4.14	0.19
1869	C/H-M	63.93	11.43	4.09	0.04	0.84	3.83	0.98	0.94	0.63	0.03	12.83	99.57	5.59	0.33
1826	C/H-M	63.64	11.71	3.00	0.02	0.63	3.65	0.80	1.08	0.63	0.03	13.43	98.62	5.43	0.33
1696	M	65.41	11.39	1.85	0.02	0.58	3.66	1.16	1.07	0.53	0.03	14.37	100.07	5.74	0.37
1695	M	66.80	11.27	1.84	0.03	0.77	3.75	0.43	1.24	0.60	0.04	13.75	100.52	5.92	0.30
1818	C/H-M	66.61	10.48	2.37	0.01	0.62	3.41	0.67	1.27	0.42	0.03	13.70	99.59	6.35	0.36
1667		66.08	11.62	3.08	0.04	0.61	3.20	0.76	1.86	0.46	0.02	12.16	99.89	5.68	0.45
1672		65.17	13.62	2.44	0.03	0.39	2.97	0.67	2.90	0.42	0.02	11.49	100.12	4.78	0.54
1661	C/H	64.58	12.64	2.69	0.03	0.79	3.34	0.67	2.43	0.49	0.04	12.83	100.53	5.10	0.48
1811	C/H	60.92	14.34	2.25	0.04	1.37	4.49	0.89	1.02	0.98	0.10	14.27	100.67	4.24	0.29
1640	C/H	55.24	12.76	7.18	0.17	2.64	6.73	0.51	1.63	0.86	0.09	13.62	101.43	4.32	0.24
1633	C/H-M	65.77	13.24	2.80	0.03	0.48	3.22	1.07	1.75	0.42	0.02	11.43	100.23	4.96	0.46
1658	M	71.30	9.23	0.86	0.01	0.45	2.90	0.45	1.34	0.36	0.02	12.45	99.42	7.72	0.38
1657	C/H-M	68.34	10.76	0.85	0.01	0.38	3.14	0.48	1.96	0.46	0.03	12.03	98.49	6.35	0.43
1621	C/H	63.53	12.44	2.98	0.02	0.78	4.38	0.98	1.05	0.47	0.05	14.39	101.07	5.10	0.31
1806	C/H-M	63.79	12.72	2.78	0.03	0.54	3.95	1.27	0.56	0.45	0.03	13.75	99.87	5.01	0.31
1805	C/H-M	63.57	11.37	3.22	0.07	0.59	3.99	1.72	0.85	0.66	0.06	12.09	98.19	5.59	0.39
1803	C/H-M	65.62	12.68	0.97	0.02	0.61	4.11	1.11	0.72	0.65	0.04	11.94	98.47	5.17	0.30
1801	M	62.92	11.85	2.88	0.02	0.84	4.06	0.84	0.95	0.55	0.04	15.76	100.71	5.30	0.30
	South														

LOI: Loss on ignition at 850ºC for 1 h
Observations: the zeolite mineralogy is indicated for those samples where XRD analyses are available for the same sample
C/H: clinoptilolite/heulandite with or without the presence of XRD traces of mordenite
C/H-M: clinoptilolite/heulandite with mordenite levels greater than trace

local hydrogeological conditions are considered to be responsible for modifying the cation/hydrogen ion ratios, favoring the formation of clinoptilolite/heulandite and mordenite in the center and south of the study area, whereas in the north, a larger volume of water circulation favored smectite formation in addition to existing clinoptilolite/heulandite.

ACKNOWLEDGMENTS

The authors are very grateful to Mr Roberto Urrutia and his artisan colleagues from Quinamávida who supported this study at the mapping stage and contributed their empirical knowledge of the tuff sequence. GEA Institute staff assistance during all stages of the analytical work is greatly appreciated. The helpful comments and recommendations by Dr F. Esenli and an anonymous reviewer are acknowledged.

REFERENCES

Accefo Ltda. (1991) *Estudio: Adopción de procesos extractivos para zeolitas chilenas en rocas volcánicas. Fondo Nacional de Desarrollo Tecnológico*. Corporación de Fomento de Producción, Santiago de Chile, Unpublished report, 78 pp.

Aguirre, L. Robinson, D., Bevins, R.E., Morata, D., Vergara, M., Fonseca, E. and Carrasco, J. (2000) A low grade metamorphic model for the Miocene volcanic sequences in the Andes of Central Chile. *New Zealand Journal of Geology and Geophysics*, **43**, 83–93.

Cabrera, R., Formas, C., Fonseca, E. and Cortón, W. (2004) *Geología y mineralogía de las zeolitas del yacimiento Lloimávida*. Unpublished report, Servicio Nacional de Geología y Minería (SERNAGEOMIN), Santiago de Chile, 17 pp.

Chipera, S.J. and Apps, J.A. (2001) Geochemical stability of natural zeolites. Pp. 117–162 in: *Natural Zeolites: Occurrence, Properties, Applications* (D.L. Bish and D.W. Ming, editors). Reviews in Mineralogy and Geochemistry **45**, Mineralogical Society of America, Chantilly, VA, and the Geochemical Society, Washington, D.C.

Christidis, G.E. (1998) Comparative study of the mobility of major and trace elements during alteration of an andesite and a rhyolite to bentonite, in the islands of Milos and Kimolos, Aegean, Greece. *Clays and Clay Minerals*, **46**, 379–399.

Cochilco – Comisión Chilena del Cobre (2004) *Anuario estadístico del cobre y de otros minerales 1985–2004*. 146 pp. www.cochilco.cl/productos/periodicos/anuario/Anuario2004.pdf

D'Gennaro, M. Cappelletti, P., Langella, A., Perrotta, A. and Scarpati, C. (2000) Genesis of zeolites in the Neapolitan Yellow Tuff. Geological, volcanological and mineralogical evidence. *Contributions to Mineralogy and Petrology*, **139**, 17–35.

Gajardo, H. (2000) Rocas y minerales industriales de Chile. *SERNAGEOMIN, Santiago de Chile, Boletín*, **58**, 181 pp.

Gottardi, G. and Galli, E. (1985) *Minerals and Rocks 18: Natural Zeolites*. Springer-Verlag, Berlin, 409 pp.

Hauser, A. (1997) Catastro y caracterización de las fuentes de aguas minerales y termales de Chile. *SERNAGEOMIN, Santiago de Chile, Boletín*, **5**, 90 pp.

Kaçmaz, H. and Köktürk, U. (2006) Zeolitas and coexisting authigenic minerals in Miocene tuffs of the Alaçati (Çeşme area) Turkey. *Clays and Clay Minerals*, **54**, 587–597.

Karzulovic, J., Hauser, A. and Vergara, M. (1979) Edades K/Ar en rocas volcánicas e intrusivas del área de los proyectos hidroeléctricos Colbún-Machicura-Melado, Empresa Nacional de electricidad, S.A., VII Región. In: *Congreso Geológico Chileno 2, Arica*, **4**, J127–J135.

Levi, B. (1969) Burial metamorphism of a Cretaceous volcanic sequence west of Santiago, Chile. *Contributions to Mineralogy and Petrology*, **24**, 30–49.

Marfil, R., La Iglesia, A., Fernández, S. and Chong-Diaz, G. (1992) Caracterización mineralógica y geoquímica de las zeolitas asociadas a tobas, riolitas y dacitas de la región de Antofagasta, Norte de Chile. *Boletín de la Real Sociedad Española de Historia Natural, Sección Biológica*, **87**, 141–153.

Moore, D.M. and Reynolds, R.C. (1997) *X-ray Diffraction and the Identification and Analysis of Clay Minerals*. Oxford University Press, New York, 378 pp.

Robinson, D. and Frey, M. (1999) *Low-grade Metamorphism*. Blackwell Science, Oxford, UK, 313 pp.

Schmid, R. (1981) Descriptive nomenclature and classification of pyroclastic deposits and fragments. Recommendations of the International Union of Geological Sciences. Subcommission on the Systematics of Igneous Rocks, *Geology*, **9**, 41–43.

Sheppard, R. and Hay, R. (2001) Formation of zeolites in open hydrologic systems. Pp. 261–276 in: *Natural Zeolites: Occurrence, Properties, Applications* (D.L. Bish and D.W. Ming, editors). Reviews in Mineralogy and Geochemistry, **45**. Mineralogical Society of America and the Geochemical Society, Washington, D.C.

Utada, M. (2001a) Zeolites in hydrothermally altered rocks. Pp. 305–322 in: *Natural Zeolites: Occurrence, Properties, Applications*. (D.L. Bish and D.W. Ming, editors). Reviews in Mineralogy and Geochemistry, **45**. Mineralogical Society of America and the Geochemical Society, Washington, D.C.

Utada, M. (2001b) Zeolites in burial diagenesis and low-grade metamorphic rocks. Pp. 277–304 in: *Natural Zeolites: Occurrence, Properties, Applications* (D.L. Bish and D.W. Ming, editors). Reviews in Mineralogy and Geochemistry, **45**. Mineralogical Society of America and the Geochemical Society, Washington, D.C.

Vergara, M. (1985) Volcanismo, Oligo-Mioceno den la Pre-Cordillera Andina del río Maule (35º 40′L.S.). Pp. 564–581 in: *Congreso Geológico Chileno 4, Antofagasta*, Vol. **4**.

Vergara, M., Levi, B. and Villarroel, R. (1993) Geothermal type alteration in a burial metamorphosed volcanic pile, central Chile. *Journal of Metamorphic Petrology,* **11**, 449–454.

Vergara, M., Morata, D., Hickey-Vargas, R.L., López-Escobar, L. and Becar, L. (1999) Tertiary tholeiitic volcanism in the Colbún area, Linares, Precordillera, central Chile (35º35′–36ºS). *Revista Geológica de Chile*, **26**, 23–41.

Vila, T. (1953) *Recursos minerales no-metálicos de Chile*. Editorial Universitaria, Santiago de Chile, 449 pp.

(*Received 8 March 2006; revised 1 June 2007; Ms. 1152; A.E. Warren D. Huff*)