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AN OCCURRENCE OF TOBERMORITE IN TERTIARY BASALTS FROM PATAGONIA, CHILE

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ABSTRACT

The hydrated calcium silicate tobermorite has been found in continental alkaline basalts of Tertiary age at Puyuhuapi, in Chilean Patagonia. Tobermorite occupies the core of amygdules, accompanied by small amounts of tacharanite, a silicate similar in composition to tobermorite. Other secondary minerals identified are phillipsite (Ba-rich variety?), which commonly occurs as a rim mineral associated with tobermorite in the same amygdule, analcime, and various Ca–Na–K zeolites. The tobermorite belongs to the 11 Å variety and is akin to the "anomalous" type, as indicated by XRD and chemical data (EPMA, SEM–EDX, ICP). Conditions of formation imply hydrothermal activity at temperatures *ca.* 150°C, involving solutions with Na, Al and a low Ca/Si value. These conditions are similar to those favoring the occurrence of tacharanite. This is the first mention of tobermorite and tacharanite in an Andean environment.

Keywords: tobermorite, tacharanite, zeolites, alkaline basalts, Tertiary, Patagonian Andes, Chile.

SOMMAIRE

Nous avons découvert la tobermorite, silicate hydraté de calcium, dans des basaltes alcalins d'affinité continentale d'âge tertiaire à Puyuhuapi, en Patagonie, au Chili. La tobermorite occupe le coeur d'amygdules; elle y est associée à la tacharanite accessoire, silicate semblable en composition à la tobermorite. Nous avons aussi identifié les minéraux secondaires suivants: phillipsite (variété riche en Ba?), répandu en bordure des cavités, analcime, et plusieurs zéolites de Ca–Na–K. La tobermorite est la variété dite de 11 Å, et ressemble à la variété "anomale", selon le spectre de diffraction X et les données chimiques (microsonde électronique, microscopie électronique à balayage, analyse par plasma à couplage inductif). Les conditions de formation impliquent une phase hydrothermale contenant Na, Al et un faible rapport de Ca à Si, et une température voisine de 150°C. Ces conditions ressemblent à celles qui favorisent la formation de la tacharanite. Il s'agit du premier exemple connu de tobermorite et de tacharanite dans un milieu andéen.

(Traduit par la Rédaction)

Mots-clés: tobermorite, tacharanite, zéolites, basalte alcalin, âge tertiaire, Andes patagoniennes, Chili.

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INTRODUCTION

Tobermorite, a rare hydrated calcium silicate, $Ca_9Si_{12}O_{30}(OH)_6 \cdot 4H_2O$, is known from only a few localities in the world, most of them in the British Isles (Claringbull & Hey 1952, McConnell 1954, Mitsuda & Taylor 1978). Tobermorite is also present in Tertiary basalts of Tasmania, where it forms dense, snow-white fillings and botryoidal encrustations in cavities. It coexists with tacharanite, a metastable member of the tobermorite family (Sutherland 1965).

We describe here the first occurrence of tobermorite in an Andean environment, where it fills amygdules in Neogene olivine basalts from the Chilean Patagonian Andes at the approximate latitude of 44°30'S. X-ray diffraction (XRD), scanning electron microscopy with energy-dispersion analysis (SEM–EDX), electron-microprobe analysis (EMPA) and inductively coupled plasma (ICP–AES) analyses have been performed with the objective to characterize this rare mineral.

PETROGRAPHY, PETROLOGY AND GEOCHEMISTRY OF THE HOST ROCKS

Rocks containing tobermorite are amygdaloidal, partly brecciated olivine basalts of probable Tertiary age composed of phenocrysts of plagioclase ($An_{75}Ab_{24}Or_1$ – $An_{72}Ab_{27}Or_1$) and fresh olivine (Fo_{83-84}) in a hyalopilitic groundmass including abundant amygdules with an average size of 3 to 5 mm and a maximum size of 20 mm, filled with various zeolites and smectite-group minerals. Outcrops of these rocks occur along the road linking Puyuhuapi with the village of La Tapera in Chilean Patagonia, approximately 48 km south of Las Juntas (Fig. 1). The basalts have an alkaline chemical affinity (Demant *et al.* 1994, Aguirre *et al.* 1997); other references to these lavas are found in Aguirre *et al.* (1994).

Secondary mineralogy

The main secondary minerals accompanying the tobermorite are zeolites, among which four compositional groups can be distinguished (Fig. 2): (a) Na-zeolites, (b) Na–Ca zeolites devoid of or poor in potassium, (c) K–Ca–Na zeolites with predominant K, and (d) Ca–K–Na zeolites with Ca as the main cation. In Figure 3, samples from group (a) plot as analcime, whereas those from group (b) define two compositional fields, one located in a position intermediate between the natrolite and mesolite end-members and characterized by a Si/Al value of 1.4 to 1.5, and the other located in the compositional space of the analcime – phillipsite solid-solutions, with a Si/Al value between 1.8 and 2.1. Zeolites from groups (c) and (d) correspond to chemical variations within the phillipsite series.

Particularly relevant among the secondary minerals is the presence of tobermorite, which appears as a milkish white mineral occupying the core in most of the amygdules and commonly surrounded by a narrow rim of phillipsite rosettes and by scattered flakes of natrolite (Fig. 4). SEM images (JSM–820 scanning electron microscope, University of Cádiz) highlight the textural contrasts between the core and the rim in these amygdules (Fig. 5a). The core is composed of spongy

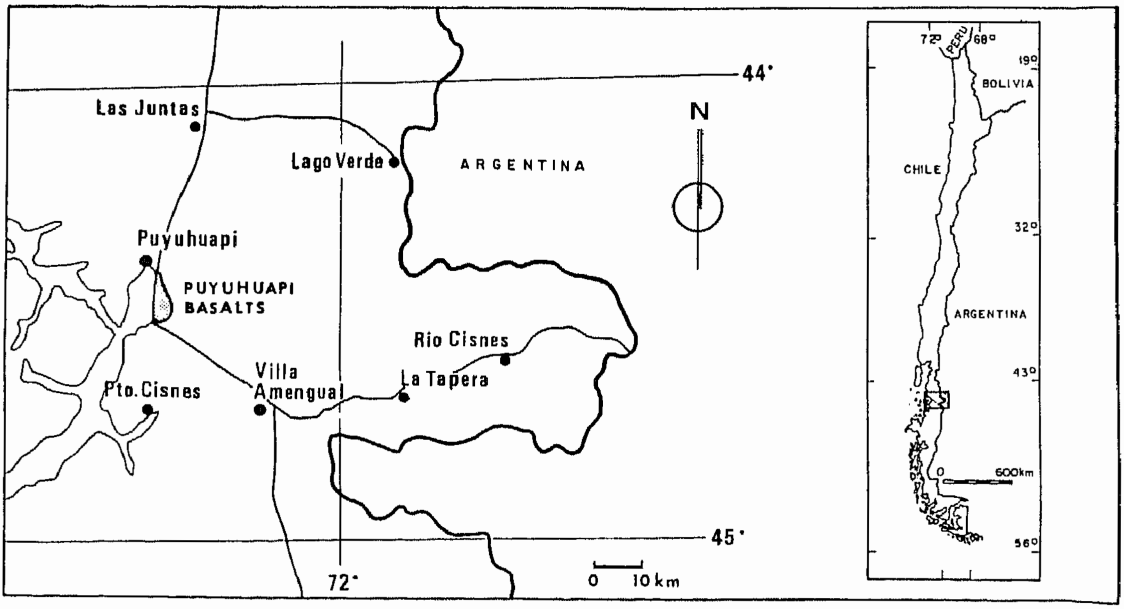

FIG. 1. Geological sketch of the Chilean Patagonian region, showing the location of the tobermorite site.

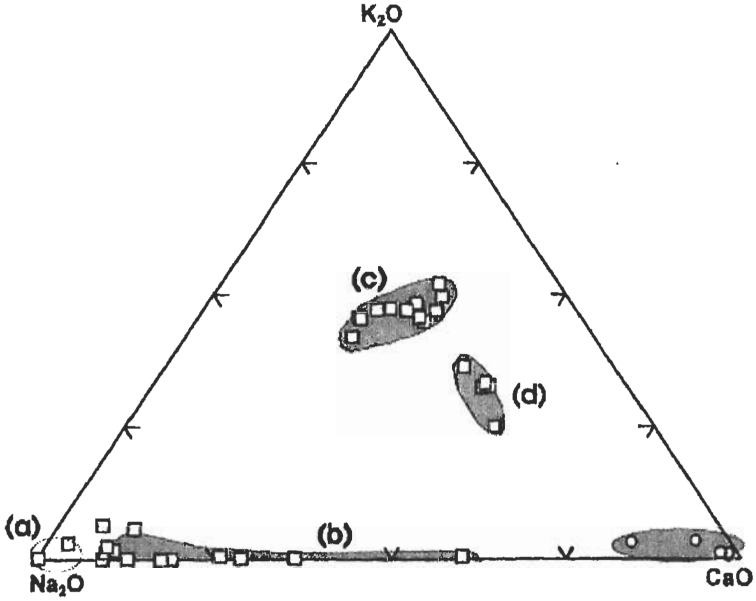

FIG. 2. CaO–K_2O–Na_2O diagram showing the compositional distribution of the secondary minerals at Puyuhuapi. Open circles: tobermorite, open squares: zeolites.

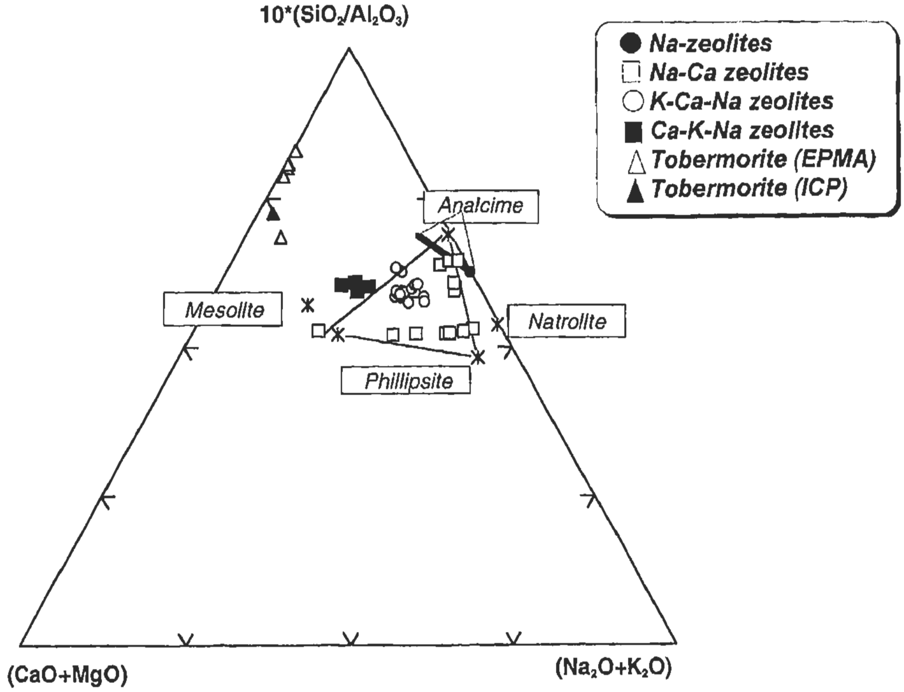

FIG. 3. (Na_2O + K_2O) – 10*(SiO_2/Al_2O_3) – (CaO + MgO) diagram used for the chemical classification of zeolites. Composition of zeolite end-members taken from Gottardi & Galli (1985). Mesolite, natrolite and phillipsite are indicated by an asterisk; the compositional range of analcime is given by a black bar.

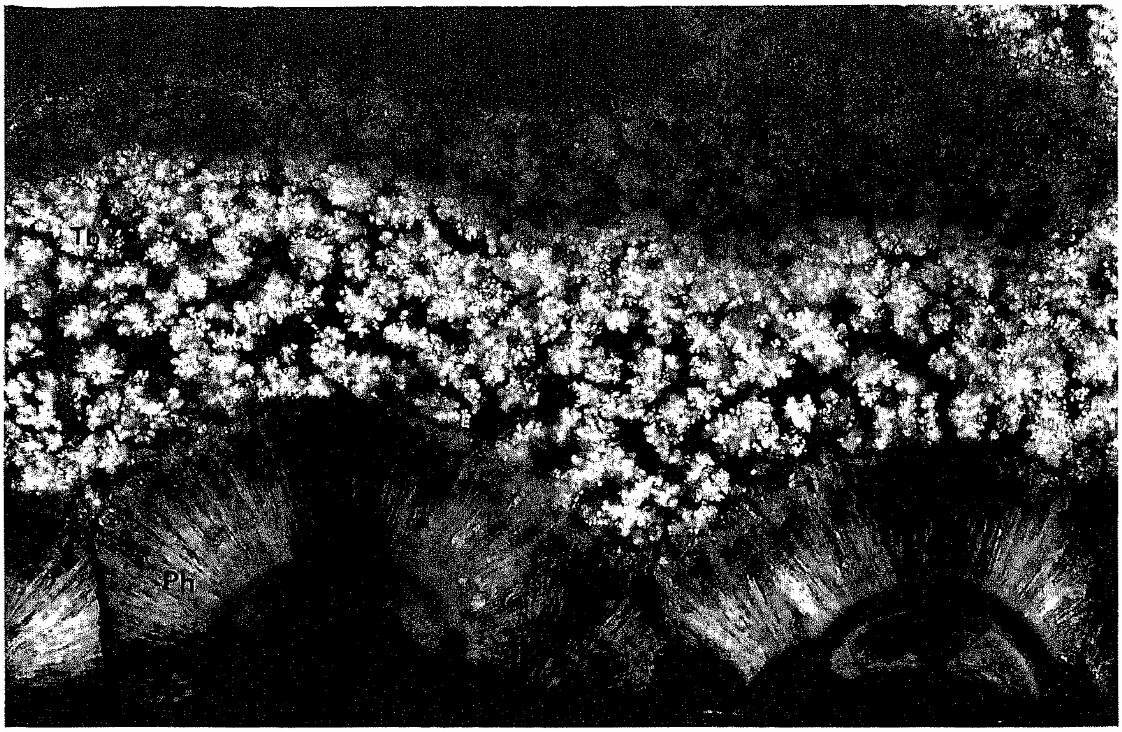

FIG. 4. Microphotograph showing the distribution of tobermorite (Tb) and phillipsite (Ph) in the interior of an amygdule (magnification = 100×).

tobermorite (Fig. 5b), lacking a defined morphology (Fig. 5c), whereas the rim is formed by idiomorphic, prismatic, crystals of phillipsite (Fig. 5d).

DATA ON TOBERMORITE

X-ray diffraction

Mineral separation was carried out to obtain concentrates of the zeolites and tobermorite in the rim and the core of the amygdules. X-ray power-diffraction data were then obtained from three different laboratories: University of Stockholm (Sweden), University of Cádiz (Spain) and University of Chile (Chile).

The main diffraction peaks of the core mineral are shown in Table 1. The principal lines of tobermorite (PDF 45–1480) correspond to *d* values at 11.3, 3.08, 2.972 and 2.806 Å, all of them clearly identified in the three diffractograms, along with the weaker lines of tobermorite. A peculiar, recurrent, peak of a *d* value between 12.618 and 12.772 Å in the diffraction patterns (Table 1), coincides with the most intense peak of tacharanite (12.7 Å in the PDF 29–0287). Other strong peaks of tacharanite (3.048, 2.775, 1.822 and 2.434 Å) also have been recorded in all the diffractograms of the core mineral.

The XRD patterns of the rim zeolite contain most of the lines characterizing phillipsite.

Chemical composition

The ideal composition of natural tobermorite is $Ca_9Si_{12}O_{30}(OH)_6 \cdot 4H_2O$. Small amounts of Na and K may replace Ca, and Al may substitute for Si to a minor extent. According to Taylor (1992), partial replacement of Si by Al is balanced by an increase in interlayer Ca, introduction of alkali cations, or both. Thus, all known naturally occurring cases of "anomalous" tobermorite [*i.e.*, having interlayer links and characterized by the fact that loss of molecules of water is accompanied by unidimensional shrinkage in the *c*-direction, according to Mitsuda & Taylor (1978)] have compositions near $Ca_4(Si_{5.5}Al_{0.5}O_{17}H_2)Ca_{0.2}Na_{0.1} \cdot 4H_2O$. Factors favoring the formation of "anomalous" tobermorite include a relatively low Ca/Si value and the presence of both Na and Al (El-Hemaly *et al.* 1977). Three distinct hydrates with a similar composition seem to exist, with a molar ratio $H_2O:SiO_2$ approximately equal to 2.5, 1.0 and 0.5, the three being present as natural products. The names plombièrite, tobermorite and riversideite have been applied to these hydrates, respectively (Hey 1962). McConnell (1954) used the name tobermorite to

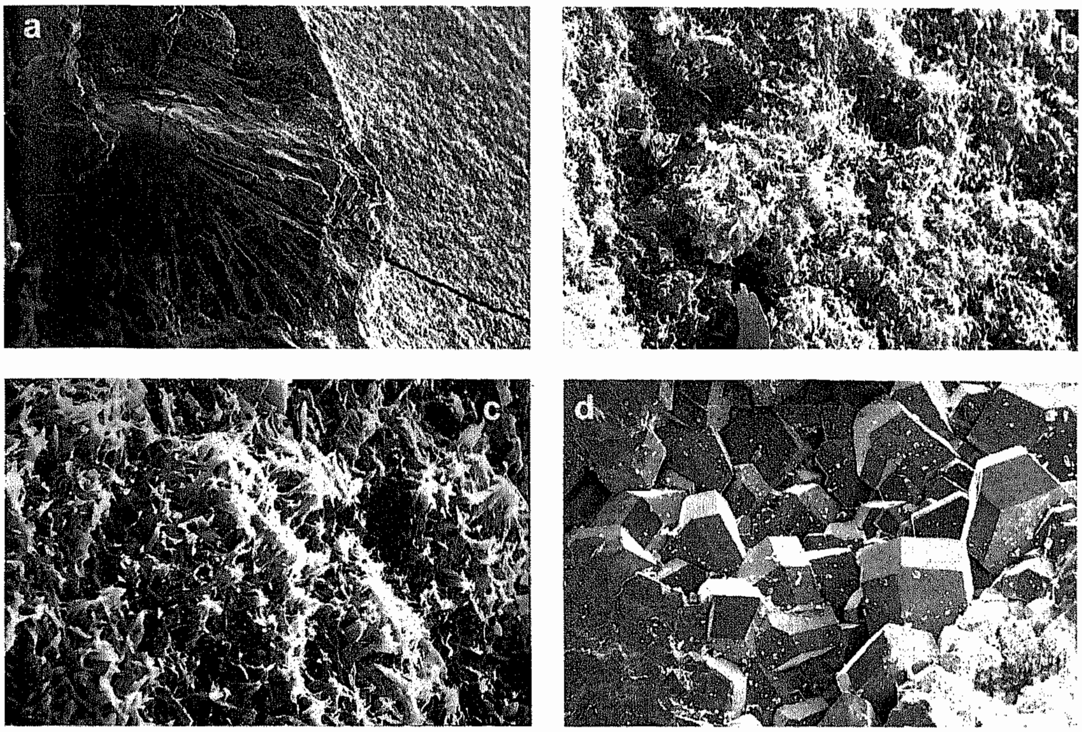

FIG. 5. SEM image of an amygdule filled by tobermorite and phillipsite. (a) General view showing the boundary zone between rim and core. Width of field of view: 0.65 mm. (b) Amygdule core composed of spongy tobermorite. Width of field of view: 40 μm. (c) Tobermorite as in (b), detail. Width of field of view: 19 μm. (d) Detail of the prismatic phillipsite at the rim of amygdules. Width of field of view: 1 mm.

describe material characterized by a 002 spacing of 11.3 Å and by a molar ratio $H_2O:SiO_2$ close to 1.0.

Synthetic tobermorite has been made free of alkalis or aluminum and with a Ca:Si value in the range 2:3 to about 3:2 (Hey 1962).

The composition of the Ca-silicate found in the basalts from Puyuhuapi, Patagonia, is given in Table 2, columns 1 to 6. Analysis 1 was performed at the Department of Geology, University of Chile by the inductively coupled plasma (ICP) method on powder obtained from the core of an amygdule in which phillipsite formed a narrow rim. Analyses 2 to 6 were carried out at the University of Montpellier, France, using a CAMEBAX electron-probe micro-analyzer (EPMA) operated at 15 kV, 0.017 mA and a beam diameter of 1 μm. The average composition obtained from the six analyses is $Ca_{3.91}Si_{5.92}Al_{0.58}O_{17}\bullet Na_{0.17}K_{0.07}$.

Chemical compositions of tobermorite from Tobermory and Loch Aynort (Skye), given in Table 2, columns 7, 8 and 9, are calculated on the basis of 17 atoms of oxygen. The average composition derived from the three analyses corresponds to $Ca_{4.0}Si_{5.5}Al_{0.49}O_{17}\bullet Ca_{0.34}Na_{0.14}K_{0.12}$.

Compared with the ideal composition of naturally occurring samples of tobermorite given above and with that of the Scottish specimens, the Ca-silicate from Patagonia is: (i) slightly deficient in Ca and devoid of interlayered Ca, (ii) enriched in Si, (iii) slightly enriched in Al, and (iv) similar in the content of interlayered cations with the exception of Ca.

The $H_2O:SiO_2$ molar ratio (H_2O calculated by difference in the analyses) in the Patagonian Ca-silicate ranges from 0.73 to 1.56 (average 0.93), which is close to 1.0, the value given as characteristic of tobermorite. The Ca:Si value is within the limits indicated above for synthetic tobermorite and is similar to the values obtained for the Scottish specimens (Table 2).

The compositions in columns 10 and 11 of Table 2 correspond to tacharanite, which is higher in Si and poorer in Ca compared to tobermorite.

DISCUSSION

According to the approximate value of its layer thickness, the tobermorite from the Puyuhuapi area corresponds to the type known as 11 Å tobermorite.

TABLE 1. MAIN *d*-VALUES OF SECONDARY MINERALS OCCURRING IN THE CORE OF AMYGDULES, PUYUHUAPI, PATAGONIA, CHILE

US		UCA		UCH		
d (Å)	r.i.(%)	d (Å)	r.i.(%)	d (Å)	r.i.(%)	Phase
12.772	24	12.618	33	12.752	26	Tcr
11.274	90	11.196	100	11.351	100	Tbm
		7.078	38	7.114	12	Tcr
5.661	17	5.656	10	5.683	6	Tbm–Tcr
5.420	24	5.409	18	5.433	15	Tbm
3.519	34	3.512	20	3.524	10	Tbm
3.299	20	3.294	20	3.289	24	Tbm
		3.188	49	3.185	18	Tcr
3.179	16	3.179	46			Tcr
3.075	100	3.077	54	3.081	62	Tbm–Tcr
		3.071	58			Tcr
3.034	51	3.036	34	3.039	36	Tcr
2.966	57	2.965	35	2.974	29	Tbm
2.897	22	2.902	23	2.923	2	Tcr
		2.858	22	2.842	11	Tcr
2.798	62	2.800	31	2.810	26	Tbm
2.719	13					Tbm?
		2.520	8			Tbm
2.501	9	2.497	8	2.501	7	Tbm–Tcr
2.431	18	2.434	12	2.444	8	Tbm–Tcr
2.298	12	2.291	8	2.302	7	Tbm
2.269	22	2.266	11	2.268	9	Tbm
2.134	13	2.132	8	2.130	7	Tbm–Tcr
2.084	14	2.082	8	2.083	8	Tbm–Tcr
		2.062	8	2.063	17	Tbm
1.997	20	1.998	10	1.997	13	Tbm–Tcr
1.844	24	1.846	10			Tbm
1.819	17	1.820	13	1.819	20	Tbm–Tcr
1.670	12	1.668	7	1.670	11	Tbm–Tcr
1.611	8			1.613	4	Tcr

The X-ray diffraction work was carried out at the University of Stockholm (US), the University of Cádiz (UCA), and the University of Chile (UCH). Symbols: Tcr: tacharanite, Tbm: tobermorite. Units: *d* values in Å, relative intensity (r.i.) in %. Equipment and operating conditions: US: PW1710 (Philips), $CuK\alpha_1$, $K\alpha_2$, 40 kV, 20 mA, 1°/min, $5° < 2\theta < 60°$. UCA: PW1820 (Philips), $CuK\alpha_1$, $K\alpha_2$, 40 kV, 40 mA, 1.2°/min, $5° < 2\theta < 70°$. UCH: D5000 (Siemens), $CuK\alpha$, 40 kV, 30 mA, 1.2°/min, $5° < 2\theta < 70°$. The samples analyzed on the three diffractometers came from the same rock fragment (hand specimen).

Moreover, these samples share various chemical and morphological features with tobermorite known as "anomalous", a name applied to tobermorite in which loss of molecular water is accompanied by unidimensional lattice shrinkage in the *c*-direction (Mitsuda & Taylor 1978). Among their chemical features, the following are particularly relevant: (i) they have significant amounts of both Al and alkalis, (ii) their cation contents are particularly low, around 4.4, and (iii) the ratio of Σcations/(Si + Al) is below the theoretical value of 0.83. Concerning their morphology, 11 Å "anomalous" tobermorite is less likely to grow easily, and mostly forms submicroscopic crystals occurring as dense, spongy, aggregates (Mitsuda & Taylor 1978). These same authors have suggested that, in the light of laboratory experiments, low Ca/(Si + Al) ratio (≤ 0.8), temperatures around 150°C, presence of both Al and alkalis tend to give "anomalous" tobermorite. This same set of conditions can be envisaged for the formation of tobermorite at Puyuhuapi.

However, some differences exist between the material from Puyuhuapi and "anomalous" tobermorite, in particular its (Si + Al) content (Table 2, columns 1 to 6). The higher Si content is attributed to the presence of small amounts of submicroscopically intergrown tacharanite in the tobermorite at Puyuhuapi (see reference compositions 10 and 11, Table 2) as indicated by the strongest reflection of this phase in the XRD pattern (Table 1). This occurrence of tacharanite in the samples would also explain the Ca values in the Puyuhuapi tobermorite (columns 1 to 6, Table 2).

Data concerning stability conditions of natural tobermorite are absent in the literature. We envisage formation of tobermorite in this Patagonian locality in a subaqueous continental environment, in connection with hydrothermal activity at volcanic centers located close to the shoreline (Demant *et al.* 1994). This hypothesis is supported by the nature of the accompanying zeolite phases, which are indicative of low-temperature alteration of rocks related to a volcanic environment. Leaching of alkaline basalts by silica-rich hydrothermal fluids produced solutions with low Ca/(Na + K) ratio, which invaded open spaces in the host rock (pores, vesicles, veinlets, vugs, etc). Precipitation of phillipsite from these solutions occurred first in small-size vesicles which were totally filled by this zeolite. In the larger cavities, a rim of phillipsite formed. A subsequent change in composition of the hydrothermal solution caused an enrichment in Ca and a depletion in Si. These changes led to the formation of tobermorite (and intergrown tacharanite, optically indistinguishable) in the core of cavities at temperatures *ca.* 150°C, according to the conditions proposed by Mitsuda & Taylor (1978).

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TABLE 2. CHEMICAL COMPOSITION OF TOBERMORITE AND TACHARANITE

	Tbm	Tbm	Tbm	Tbm	Tbm	Tbm	Tbm	Tbm	Tbm	Tcr	Tcr
	Puyuhuapi						Tobermory		LA	Bramberg	Huntly
	1	2	3	4	5	6	7	8	9	10	11
SiO_2 wt.%	44.17	50.45	51.46	49.52	50.41	51.50	46.51	46.62	46.17	48.30	48.50
TiO_2	0.02	0.01	0.06	0.09	0.05	0.17					
Al_2O_3	5.70	3.16	3.72	3.87	3.59	4.38	2.40	3.90	4.26	4.50	5.50
FeOt	0.02	0.92	0.85	1.27	1.29	1.34	2.88	1.68	0.15	0.00	0.00
Cr_2O_3	0.00	0.00	0.00	0.01	0.00	0.00					
MnO	0.02	0.03	0.03	0.01	0.03	0.04					
MgO	0.00	0.49	0.50	0.74	0.74	0.85	0.47	0.00	0.00	0.40	0.00
CaO	27.00	32.01	32.09	30.67	32.82	30.62	33.40	33.98	35.15	30.80	30.00
Na_2O	1.40	0.49	0.55	0.69	0.45	0.74	0.36	0.89	0.56	0.50	0.00
K_2O	1.04	0.24	0.32	0.41	0.38	0.39	1.45	0.57	0.25	0.60	1.00
H_2O	20.65	13.12	11.27	13.99	11.53	11.31	12.61	12.11	13.47	14.90	14.90
Total	100.02	100.92	100.85	101.27	101.29	101.34	100.08	99.75	100.01	100.00	99.90

Structural formulae on the basis of 17 atoms of oxygen

	1	2	3	4	5	6	7	8	9	10	11
Si *apfu*	5.752	5.985	5.967	5.926	5.896	5.948	5.562	5.470	5.472	5.906	5.910
Ti	0.002	0.001	0.005	0.008	0.004	0.015					
Al	0.875	0.442	0.508	0.546	0.495	0.596	0.338	0.539	0.595	0.649	0.790
Fe^{3+}	0.098	0.089	0.087	0.090	0.088	0.087	0.288	0.165	0.015	0.000	0.000
Cr	0.000	0.000	0.000	0.001	0.000	0.000					
Mn	0.002	0.003	0.003	0.001	0.003	0.004					
Mg	0.000	0.087	0.086	0.132	0.129	0.146	0.084	0.175	0.177	0.073	0.000
Ca	3.767	4.068	3.987	3.932	4.113	3.789	4.279	4.271	4.463	4.035	3.917
Na	0.353	0.113	0.124	0.160	0.102	0.166	0.083	0.202	0.129	0.119	0.000
K	0.173	0.036	0.047	0.063	0.057	0.057	0.221	0.085	0.038	0.094	0.155
Total	11.022	10.824	10.815	10.859	10.887	10.808	10.855	10.907	10.888	10.875	10.773
Si/Al	6.575	13.547	11.738	10.858	11.915	9.977	16.444	10.144	9.197	9.107	7.482
$(H_2O/SiO_2)_{molar}$	1.561	0.868	0.731	0.943	0.764	0.733	0.905	0.867	0.974	1.030	1.026
Ca/Si	0.655	0.680	0.668	0.664	0.698	0.637	0.769	0.781	0.816	0.683	0.663
Σcations	4.396	4.397	4.340	4.387	4.496	4.264	4.955	4.899	4.821	4.320	4.072
Si + Al	6.627	6.426	6.476	6.472	6.391	6.544	5.900	6.009	6.067	6.555	6.700
Σcations/(Si+Al)	0.663	0.684	0.670	0.678	0.703	0.652	0.840	0.815	0.795	0.659	0.608

Column 1: tobermorite, Puyuhuapi, ICP (University of Chile, J. Martinez, analyst); columns 2 to 6: tobermorite, Puyuhuapi, EPMA (Université de Montpellier, France); columns 7 to 9: tobermorite, Tobermory, Isle of Mull and Loch Aynort (LA), Isle of Skye (Claringbull & Hey 1952); columns 10 and 11: tacharanite, Bramburg, Germany, and Huntly, Isle of Skye, U.K. (Cliff *et al.* 1975). In all cases, iron is expressed as Fe_2O_3. Structural formulae are expressed in atoms per formula unit (*apfu*). Symbols: Tbm: tobermorite, Tcr: tacharanite.

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