GEOLOGICAL NOTE

Mineralogical investigations of agates from Cordón de Lila, Chile

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ABSTRACT. In the present study a first found of agates in Chile is reported from the Cordón de Lila region in northern Chile. The agates occur as veins and lenses in altered Permian volcanic rocks. The rock composition is rhyodacitic/dacitic consisting of a fine-grained K-feldspar-quartz groundmass with phenocrysts of plagioclase (An_{50-60}) and pyroxene (augite). The volcanic host rocks show strong features of alteration and brecciation. Results of XRD, polarizing microscopy and cathodoluminescence (CL) microscopy and spectroscopy point to a late- to postvolcanic formation of the agates by hydrothermal fluids and SiO_2 which was released during the alteration of unstable minerals and volcanic glass. Strongly varying agate micro-textures and the appearance of euhedral quartz crystals with µm-sized growth lamellae (so called Bambauer quartz) indicate fluctuations in the physico-chemical conditions (SiO_2 concentration, pH) during alteration and agate formation. Another indication for the alteration processes is the occurrence of secondary calcite in the agate-bearing rocks.

Keywords: Cordón de Lila, Volcanic rocks, Mineralogy, Geochemistry, Agate.

RESUMEN. Investigaciones mineralógicas de ágatas del Cordón de Lila, Chile. En el presente trabajo se realiza el primer estudio de ágatas en Chile, procedentes del Cordón de Lila. Las ágatas se presentan como vetas y lentes en rocas volcánicas alteradas del Pérmico. La composición de la roca huésped es riodacítica a dacítica y consiste en una masa fundamental de grano fino de feldespato potásico y cuarzo con fenocristales de plagioclasa (An_{50-60}) y piroxeno (augita). Se observa una intensa alteración y brechización de la roca huésped. Se realizaron estudios de difracción de rayos-X, microscopio polarizado y catodoluminiscencia (CL) que indican un origen posvolcánico para las ágatas, las que se formaron a partir de fluidos hidrotermales y sílice liberada durante la alteración de minerales inestables y vidrio volcánico. La notoria variación de la microtextura de las ágatas y la presencia en ellas de cristales euhedrales de cuarzo con láminas de tamaño micrométrico (cuarzo de tipo Bambauer) indican variaciones en las condiciones físico-químicas que consisten en concentración de sílice y variaciones de pH durante la alteración y formación de las ágatas. Otro indicio de procesos de alteración es la presencia de calcita en la roca huésped de estas.

Palabras clave: Cordón de Lila, Rocas volcánicas, Mineralogía, Geoquímica, Ágatas.

1. Introduction

Agates are spectacular products of nature, which are to be found all over the world in different geological environments. From a textural point of view agate is banded chalcedony incorporating certain other SiO_2 polymorphs and varieties (*e.g.*, Heaney, 1993; Graetsch, 1994; Moxon, 1996; Götze *et al.*, 1998; Moxon and Ríos, 2004). Other minerals such as Fe-oxides or carbonates are frequently intergrown with the SiO_2-minerals pointing to complex processes of agate formation.

Agates most frequently formed in SiO_2-rich (rhyolite, rhyodacite) and SiO_2-poor (andesite, basalt) volcanic rocks. Many authors assume that the formation of volcanic agates is associated with late- or post-volcanic alteration or weathering of volcanic host rocks (*e.g.*, Harder, 1993; Pabian and Zarins, 1994; Pabian and Zarins, Möckel and Götze, 2007; Götze, 2011). Alternatively, agates may also form as hydrothermal vein agates in fissures and fractures of crystalline rocks, or from low-temperature SiO_2-rich solutions in pores and cavities of sedimentary rocks (Götze, 2011).

Volcanic agates were reported from different localities in southern America (*e.g.*, Brazil, Uruguay, Argentina, Perú), in particular related to basic and intermediate volcanic rocks. For instance, in the Andean regions of Argentina (Patagonia and San Rafael, Mendoza) famous occurrences of agates exist (Zenz, 2005). Although Chile is a country which is widely dominated by the Andean Cordillera with manifold volcanic activities, no agates were described in Chile up to now. The present paper presents first agate founds in the northeast of Chile (Cordón de Lila region) and provides a basic mineralogical and geochemical characterization of the agates and the related agate-bearing volcanic rocks.

2. Geological Setting

The agate samples originate from the Permian Cerro Negro Formation in Cordón de Lila, northeast of Chile (Niemeyer, 1989, 2013). These rocks are the result of the subduction of an oceanic plate (Nazca plate) under the continental South American plate. Cordón de Lila consists of two blocks, a western and an eastern one, which are separated by the Tucucaro Fault (Fig. 1). These parts show differences in the geological composition. First occurrences of agates were found at the basal Cerro Negro Formation, which is situated within the eastern block (number 7 in figure 1).

The geological unit consists of a 400 m thick volcanic succession with certain sedimentary sub-layers (Muñoz, 2009). This formation is the uppermost stratified unit of the eastern block. The volcanic activities occurred during Permian and covered small areas. The western part of the Cordón de Lila is covered by granitic batholiths resulting in lacking surface exposure of volcanic rocks near the sample location.

Agates were found within Permian volcanic rocks in a location close to the border of the western and eastern block at 23°52'06'' S and 68°22'15'' W (Fig. 1).

3. Materials and Methods

3.1. Sample material

Out of a total of five samples, four (CH 1-4) were chosen for further investigations (Fig. 2). Sample CH1 is an agate breccia. It consists of a white matrix with a few centimeters long brownish to greenish-brown fragments. At the rim of the breccia, the contact to the host rock is visible (Fig. 2A).

Samples CH2-CH4 represent lithophysae of the volcanic host rock and differ markedly from sample CH 1 (Fig. 2B-D). The volcanic rocks show a porphyric texture with phenocrysts (3-4 mm) within a fine-grained, brown matrix. The agate zones itself are enclosed in small (<2 cm), SiO_2-filled veins or appear as larger, oval areas (Fig. 2B).

Polished thin sections were prepared from samples CH 1-4 for microscopic investigations and cathodoluminescence (CL) studies. Additional sample material was selected for further chemical and mineralogical investigations. The rock material was crushed to <400 μm and aliquots were milled to a fraction <63 μm for geochemical analysis and 2-4 μm using a McCrone micronizing mill for X-ray diffraction (XRD) studies, respectively. The latter powder was mixed with 20 mass-% Al_2O_3 as internal standard for quantitative XRD measurements.

3.2. Analytical methods

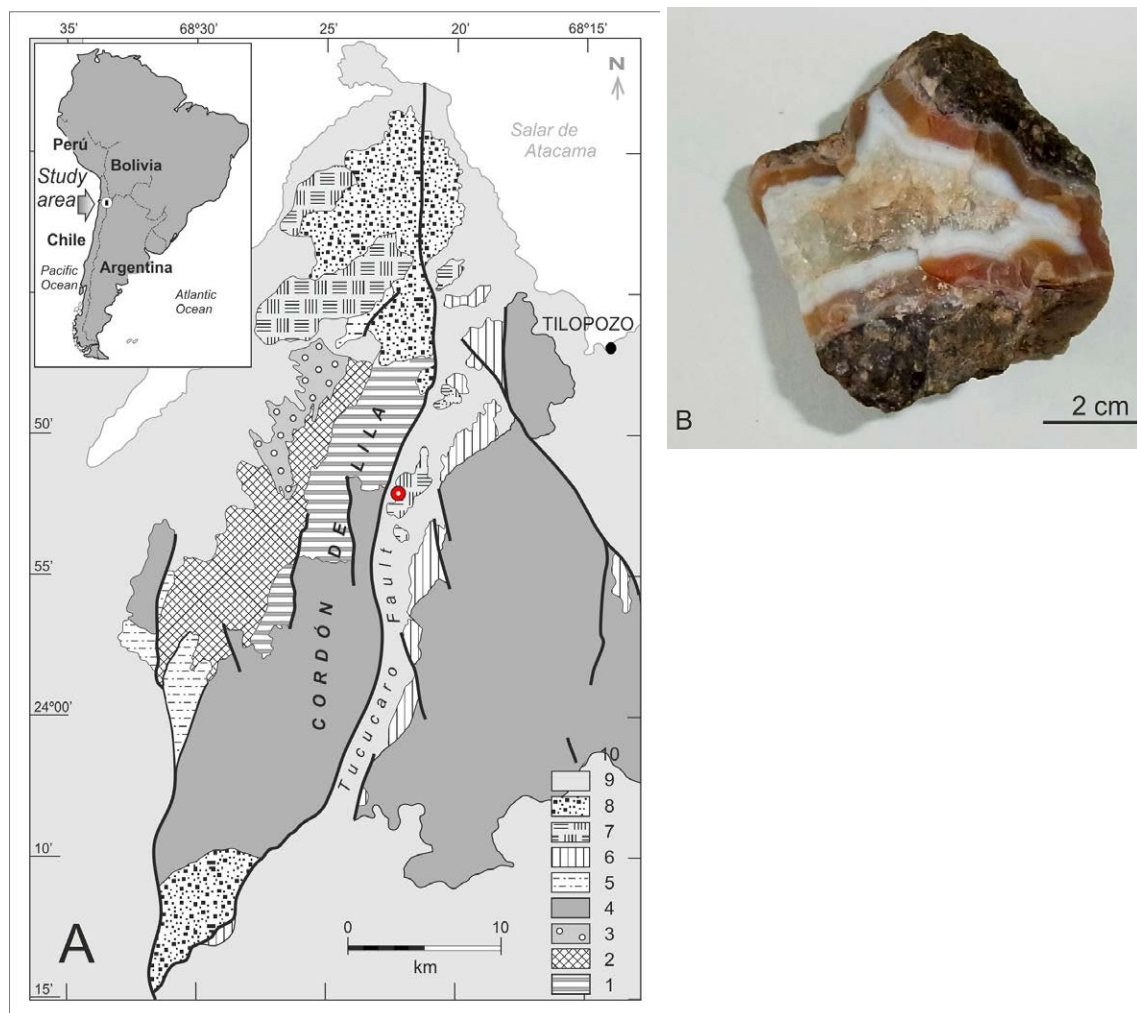The whole rock composition of the samples was investigated by chemical analyses using X-ray

FIG. 1. **A.** Geology of Cordón de Lila with location of the agate samples (red dot) from the study area: 1. Cordón de Lila Complex (CISL), Lower Member: basalt and turbidite (Ordovician); 2. Cordón de Lila Complex (CISL), Upper Member: dacite and dacitic volcanic breccia (Ordovician); 3. Quebrada Grande Formation: conglomerate and sandstone (Ordovician); 4. Granitoid (Ordovician); 5. Quebrada Ancha Formation: quartzarenite (Silurian); 6. Lila Formation: sandstone and conglomerate (Devonian); 7. Cerro Negro Formation: dacite and andesite with sublayers of sandstone (Permian); 8. Granitoid (Upper Paleozoic); 9. Alluvium; 10. Fault; **B.** Agate sample.

fluorescence (XRF). Fused pellets were made from 1 g of calcinated material mixed with 8g lithium-tetraborate ($Li_2B_4O_7$). The measurements were done with a Panalytical Axios Minerals XRF device, equipped with a 4 kW Rhodium X-ray tube. The measurements were evaluated using the Panalytical Software package SuperQ.

The mineral composition of powdered samples was analyzed in aluminum sample holders with an X-ray diffractometer URD6 (Seifert/Freiberger Präzi-

sionsmechanik) with CoKα radiation (40kV/30mA). The irradiated area was kept constant at 15mm². Measurements were conducted in the range between 5-80° 2 θ with steps of 0.03° 2θ and an accumulation time of 2sec/step. The resulting X-ray diffractograms were quantified using AutoQuan/BGMN (Bergmann *et al.*, 1998).

Polarizing microscopy investigations were carried out using an Axio Imager 1 m (Carl Zeiss) equipped with a MRc5 digital camera. In addition, cathodo-
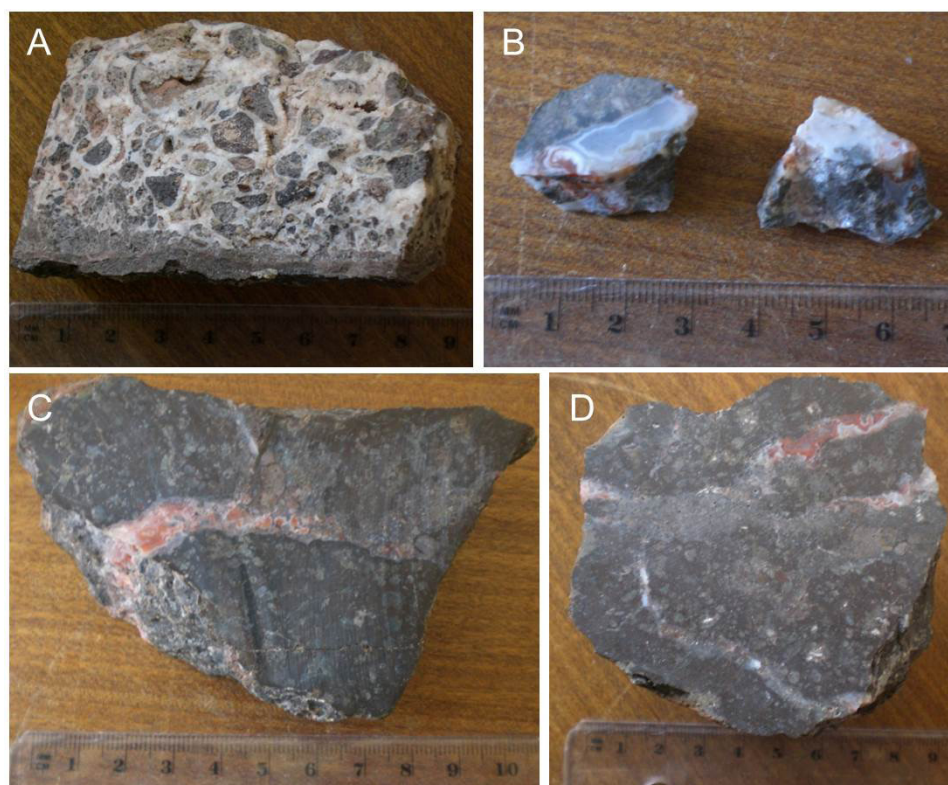
FIG. 2. Investigated samples of the present study. **A.** CH1, agate-breccia; **B.** CH2, bluish agate in host rock; **C.** CH3, small lithophyse; **D.** CH4, large lithophyse.

luminescence (CL) microscopy and spectroscopy studies were made on carbon coated polished thin sections. The CL microscope was a "hot cathode" CL microscope HC1-LM, which used an acceleration voltage of 14 kV and a beam current of 0.2 mA (Neuser *et al*., 1995). Images were taken with an Olympus DP72 digital camera. CL spectra in the wavelength range of 380-900 nm were recorded with an Acton Research SP-2356 spectrograph, which was linked to the microscope via an optical glass-fibre guide. CL spectra were recorded under standardized conditions with a spot size of about 30 µm in diameter by using a pinhole aperture. An Hg-halogen lamp was used for wavelength calibration.

4. Results

4.1. Mineralogy and geochemistry of host rocks

The chemical and mineralogical composition of the investigated host rocks is presented in Tables 1 and 2.

Samples CH-2 to CH-4 represent acidic volcanic rocks with SiO_2 contents between 64.5 and 66.3 wt%. This is also shown in the mineral composition, which is dominated by quartz, sanidine and plagioclase. XRD data revealed two types of sanidine. The amount of amorphous material (*e.g.*, volcanic glass) is remarkable and varies between 5.4 and 14.6 wt%. In addition, considerable amounts of smectite and vermiculite were detected.

In contrast, the SiO_2 content of sample CH-1 is much higher (84.8 wt%) and indicates a high amount of secondary silica. In general, the breccia is a mixture of quartz and calcite, and only 8.6 wt% sanidine were detected.

4.2. Micro-texture and cathodoluminescence (CL)

Microscopic investigations showed that the matrix of sample CH-1 mainly consists of fine- to medium-grained quartz. Residues of dark, strongly altered phenocrysts (up to mm in size) are embed-

TABLE 1. CHEMICAL COMPOSITION OF INVESTIGATED HOST ROCKS DETERMINED BY XRF (IN wt%).

	CH-1	CH-2	CH-3	CH-4
SiO_2	84.8	66.3	64.5	66.0
TiO_2	0.23	0.67	0.83	0.75
Al_2O_3	2.90	12.1	13.4	13.3
Fe_2O_3	1.49	4.33	5.37	4.92
Mn_3O_4	-	0.08	0.08	0.08
MgO	-	1.53	1.19	0.94
CaO	3.32	2.38	3.08	3.18
Na_2O	-	1.47	1.75	1.95
K_2O	1.46	5.72	5.77	4.88
BaO	-	0.13	0.16	0.13
CuO	-	-	0.03	-
LoI	3.59	1.83	1.45	1.33
Σ	97.79	96.54	97.61	97.46

TABLE 2. MINERAL COMPOSITION OF INVESTIGATED HOST ROCKS FROM XRD STUDIES (IN wt%).

	CH1	CH2	CH3	CH4
Quartz	79.1	27.9	24.5	28.0
Sanidine	8.6	32.3	36.0	30.6
Plagioclase	-	18.1	19.4	26.0
Calcite	3.9	-	-	-
Hematite	0.9	0.7	1.4	2.1
Smectite	-	3.8	4.4	3.9
Pyroxene	-	2.7	4.5	3.5
Vermiculite	-	-	-	0.5
Amorphous	7.5	14.6	9.9	5.4

ded within the matrix, sometimes together with iron oxides. Because of the strong degree of alteration and the small grain size it was not possible to identify the mineral composition of the phenocrysts (probably residues of feldspars).

Euhedral, prismatic quartz crystals are also grown in small cavities showing orientations inwards the holes (Fig. 3A). These crystals exhibit a short-lived blue CL colour and distinct growth and sector zoning (Fig. 3B). Crystals of calcite are dispersed in the quartz matrix, sometimes forming clusters of large crystals (Fig. 3C). They show a yellow to orange CL colour (Fig. 3D), which is a result of activation by Mn^{2+} replacing Ca^{2+} in the calcite structure (Götze, 2012).

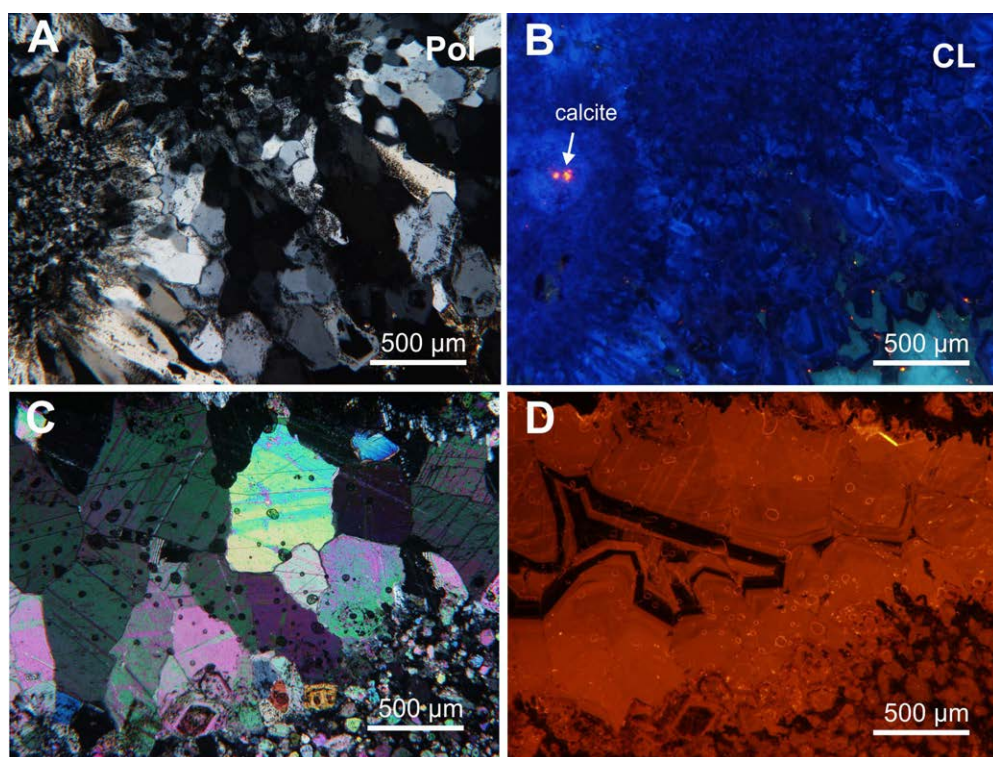Samples CH-2-4 show a typical porphyric texture with a fine-grained matrix and large phenocrysts

FIG. 3. Microscopic textures of sample CH-2 (agate breccia) in polarized light (Pol) and cathodoluminescence (CL). **A.** Quartz matrix in polarized light with euhedral cystals grown in cavities; **B.** Quartz shows short-live blue CL and distinct zoning; **C.** Coarse-grained calcite crystals with pressure twinning; **D.** Calcite exhibits orange-yellow CL and distinct zoning.

of plagioclase and pyroxene (Fig. 4). CL studies revealed that the fine-grained matrix consists mainly of K-feldspar and quartz, which both do not appear as large crystals.

Most of the phenocrysts are plagioclases showing polysynthetic twinning in polarized light and greenish CL colour with growth zoning. Chemical analyses with SEM-EDX revealed variations in the chemical composition of the plagioclases between 3.8 and 5.2 atom-% Ca and 2.9 and 4.0 atom-% Na. In addition with results from CL spectroscopy we calculated plagioclase compositions of An_{50-60}. The plagioclase crystals are often strongly altered and small areas of kaolinite (deep blue CL) were detected as alteration product.

Pyroxene phenocrysts also show strong features of alteration. Some of the crystals completely lost their characteristic properties. Nevertheless, pyroxene crystals could be identified based on their optical properties as augite. Accessory minerals detected in samples CH-2-4 are apatite, zircon and iron oxides.

Another feature of samples CH-2-4 is the presence of agate as well as fissures and veins of secondary quartz. The quartz fissures crosscut not only the rock matrix but also large crystals of plagioclase (Fig. 5) emphasizing the secondary origin of this generation. A conspicuous feature is the occurrence of small, μm-sized lamellae in euhedral quartz crystals (Fig. 6). According to the first description by Bambauer *et al*. (1961) these growth phenomena are called Bambauer quartz. This secondary type of quartz shows short-lived blue CL.

4.3. Agate/chalcedony

The agate mineralization macroscopically consists mainly of wall-banded chalcedony layers of yellow to white, orange-red and pale blue coloration as well as macro-crystalline quartz (compare figures 1 and 2).

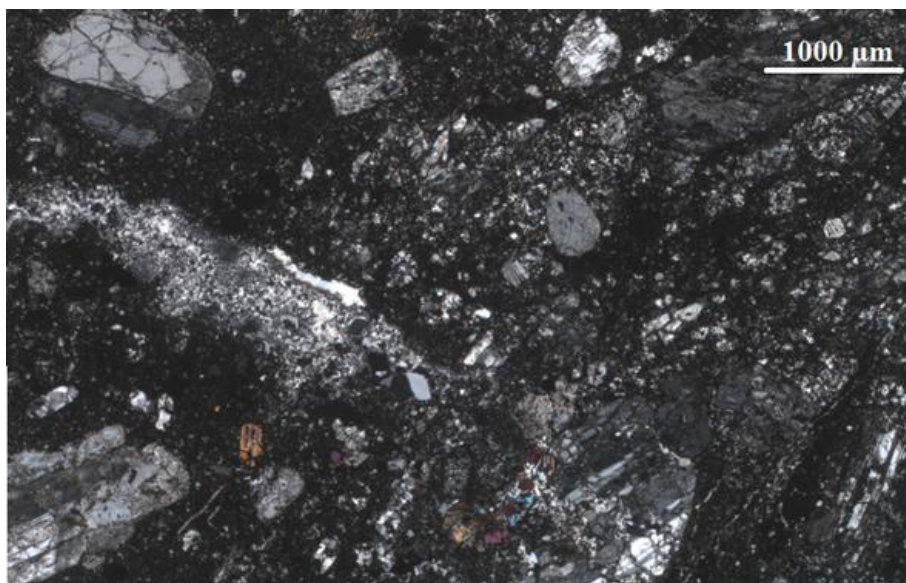Microscopic investigations revealed that chalcedony shows differing grain sizes and morphology

FIG. 4. Polarized light micrograph showing the typical porphyric texture of sample CH-2; phenocrysts of plagioclase and pyroxene are embedded in a fine-grained matrix of quartz and K-feldspar; a secondary quartz veinlet is crosscutting the rock.
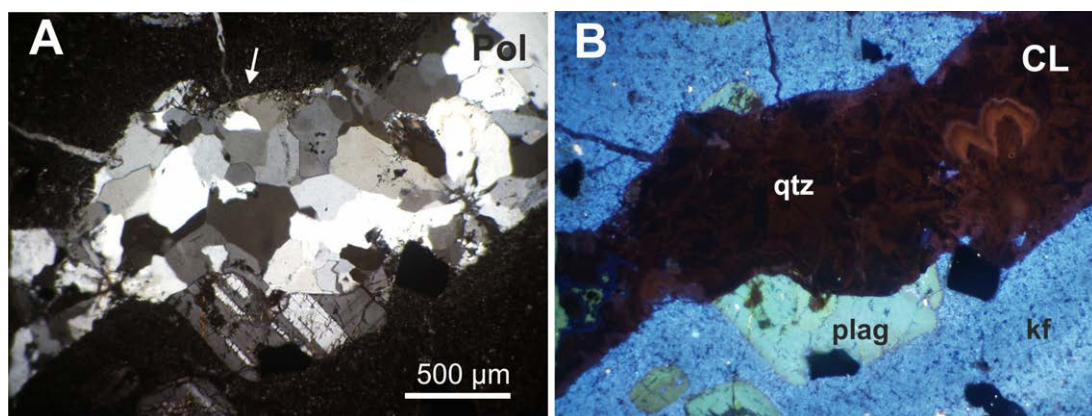

FIG. 5. Secondary generation of quartz (qtz) in sample CH-3 crosscutting the matrix of fine-grained K-feldspar (kf) and quartz as well as plagioclase phenocrysts (plag). **A.** polarized light (Pol); **B.** cathodoluminescence (CL).

(granular and fibrous, Fig. 7), and is sometimes intimately intergrown with other SiO_2 modifications and/or varieties such as quartz and quartzine (Fig. 8). Quartzine is intercalated between chalcedony bands and was identifiable by the different orientation of the quartz crystallites compared to chalcedony (Fig. 8). Hematite impurities (up to several µm in size) are commonly found in the chalcedony matrix.

Results of CL studies show details of the agate micro-texture partly consisting of different chalcedony

generations. These generations are visible by their varying luminescence properties (see arrows in figure 7D). In some cases agate is directly associated with quartz showing short-lived blue CL.

5. Discussion

The host rocks of the agates in the present study were clearly identified as volcanic rocks due to their typical porphyric texture. The rocks mainly consist of
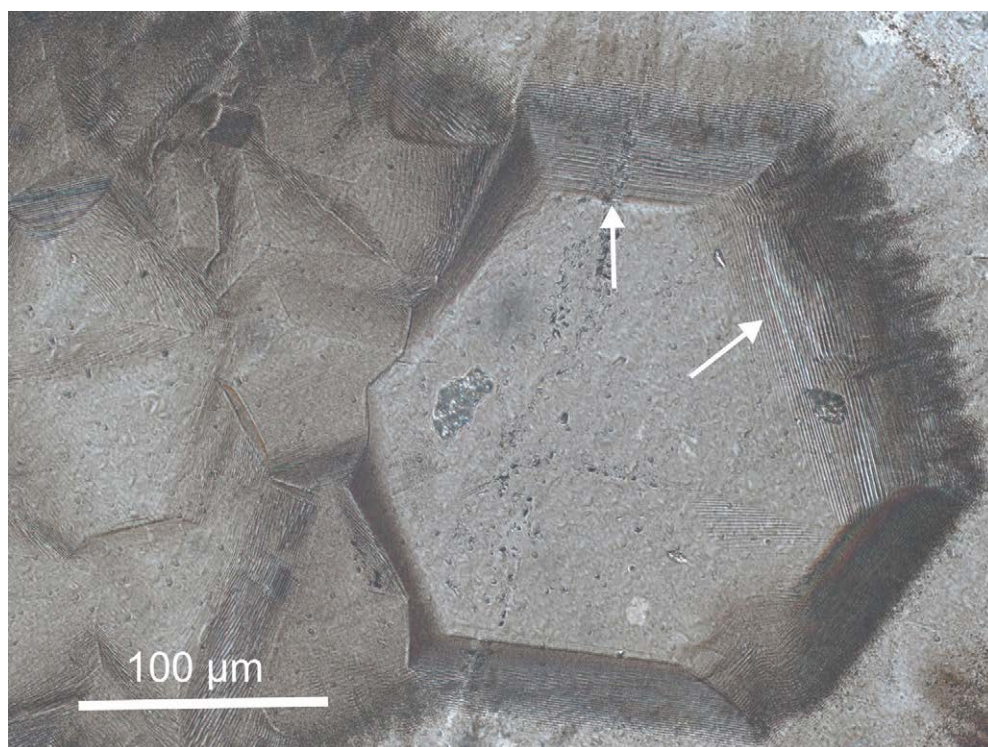
FIG. 6. Euhedral crystals of secondary quartz in sample CH-2 showing µm-sized growth lamellae (arrows), so-called Bambauer quartz.

a fine-grained groundmass of K-feldspar and quartz with phenocrysts of plagioclase (An_{50-60}) and pyroxene (augite). Based on the geochemical signature, the rocks plot into the rhyodacite/dacite field of the SiO_2-Zr/TiO_2-diagram according to Winchester and Floyd (1977) (Fig. 9).

The host rocks show strong features of alteration. Pyroxene is strongly altered and plagioclases also contain typical alteration products such as secondary carbonate (calcite) and kaolinite. Additional evidence for a hydrothermal overprint of the volcanic host rocks is provided by the occurrence of smectite and vermiculite (compare Table 2). Both are typical hydrothermal alteration products of volcanic materials. Sample CH-1 represents an agate breccia, which is probably the product of both mechanical and chemical overprint of the primary volcanic rocks. The breccia mainly consists of calcite and secondary quartz. The hydrothermal origin of this quartz was proved by the typical short-lived blue CL (Götze, 2012).

Information concerning the physico-chemical conditions could also be drawn from the occurrence of hydrothermal Bambauer quartz with typical growth lamellae (Fig. 6). According to Rykart (1989) the formation of such lamellae is related to low temperature hydrothermal conditions with strong fluctuations in silica concentration and pH conditions. These fluctuations are probably also the reason for the manifold forms of appearance of different SiO_2 phases within the agates (Fig. 7). There are strong indications for several agate generations from the CL studies (*e.g.*, Fig. 7C-D).

The common occurrence of hydrothermal quartz and agate point to the same silica source for the mineralisation processes. Since agates occur in lithophysae, breccia and veins within the same geological context, it is obvious that agate forming fluids filled both existing cavities and replaced solid rocks. Accordingly, the agate-forming process can be related to late- or post-volcanic hydrothermal processes which resulted in a strong alteration of the volcanic host rocks. The SiO_2 for silicification can both originate from magmatic-hydrothermal fluids and silica which was released during the alteration of primary minerals and volcanic glass from the groundmass.
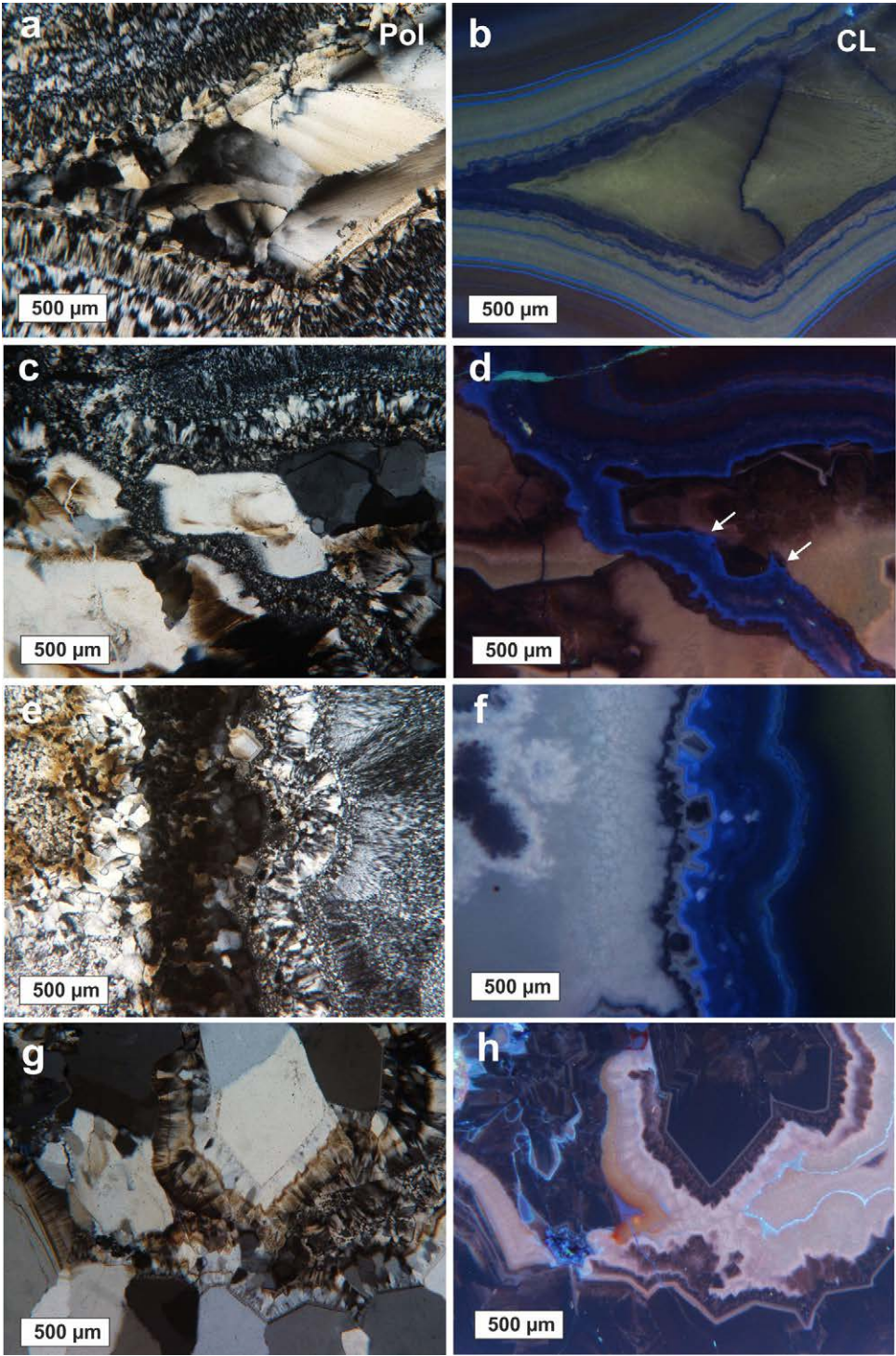
FIG. 7. Polarized light-CL micrographs of agate features in samples CH-2 (A-D) and CH-3 (E-H). **A-B.** Multi-coloured chalcedony bands in CL showing differences in grain size and texture; **C-D.** Different generations of silica; a late generation (blue CL-see arrows) is penetrating earlier quartz; **E-F.** Different types of chalcedony (granular and fibrous) showing different luminescence colours; **G-H.** Different generations of macro-crystalline quartz and chalcedony indicating changes in growth conditions.
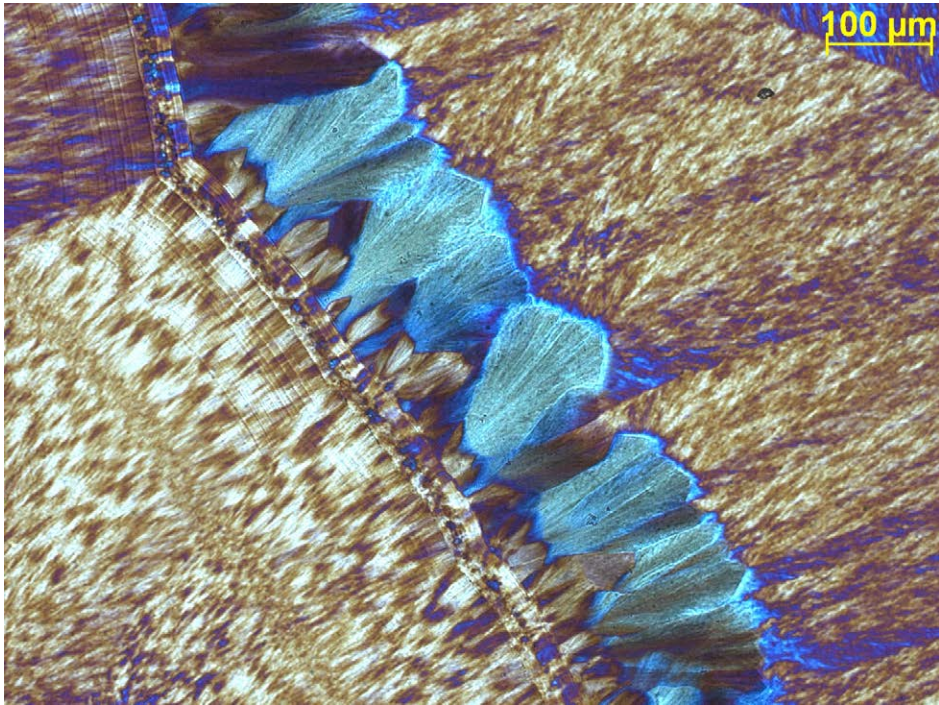
FIG. 8. Polarized light micrograph with additional nγ/λ compensator showing a quartzine layer (bluish) intercalated between chalcedony layers (yellow) within agate of sample CH-2.
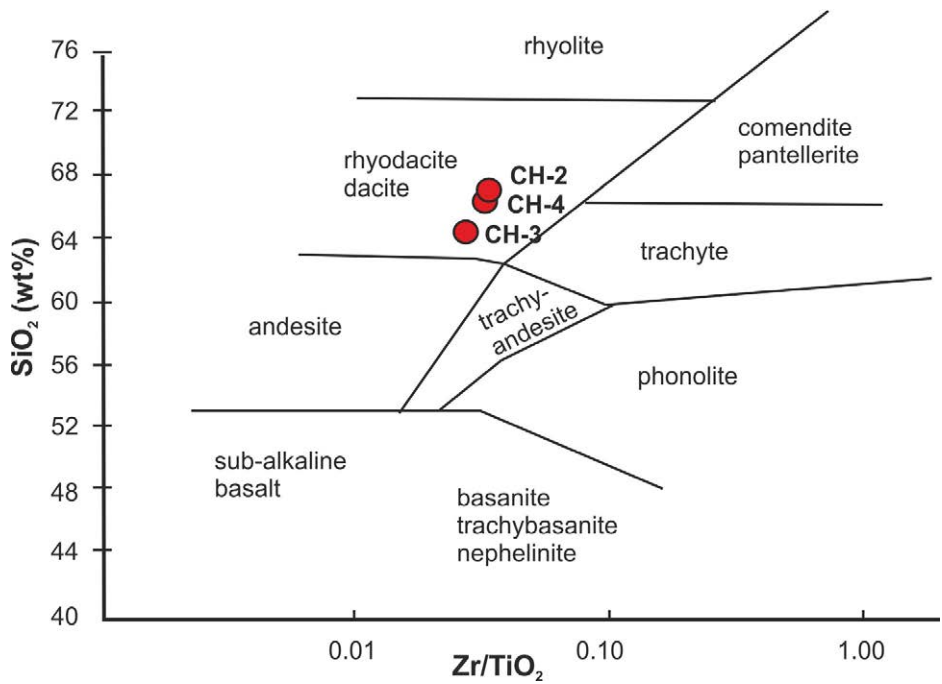

FIG. 9. Classification of the investigated volcanic rocks (red dots) according to Winchester and Floyd (1977).

6. Conclusions

The present study first presents data about the occurrence of agates in volcanic rocks from the Cordón de Lila region in northern Chile. Agates from Chile were unknown so far, although the geological environment is favourable for agate formation and agate occurrences have been reported from other Andean countries such as Argentina.

The results of the study show that agates occur in rhyodacites/dacites which have undergone late- to post-volcanic hydrothermal alteration. The silica necessary for agate formation probably derives both from hydrothermal fluids and SiO_2 which was released during the alteration of unstable minerals and volcanic glass. Different agate micro-textures and the appearance of Bambauer quartz point to remarkable fluctuations in the physico-chemical conditions (SiO_2 concentration, pH) during altera- tion and agate formation.

Acknowledgements

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