

Structural hydroxyl contents of nominally anhydrous minerals in the Miocene Laleaua Albă magmatic complex (East Carpathians, Romania): Benchmarks for the water content of parent melts

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Abstract: The Laleaua Albă (White Tulip) magmatic complex (LA) consists of small-scale composite andesitic–dacitic dikes representing the third volcanic phase (8.5–8.0 Ma) of the Gutâi Volcanic Zone (GVZ) within the Neogene–Quaternary volcanic chain of the East Carpathians (Romania). The LA comprises two composite dikes that crosscut older volcanic units. The outcrop, at the sampling site exhibit a tulip-shaped light-colored dacitic core – containing abundant mafic microgranular enclaves (MME) – surrounded by a dark gray andesitic envelope. Volcanic rocks from the GVZ and LA display typical post-collisional (calc-alkaline) geochemical signatures. Based on their major element compositions, the studied clinopyroxenes are primitive (Mg#: 73–85) and represent the earliest crystallization phases. Clinopyroxene geothermobarometry indicates crystallization pressures of ~5.5–8.5 kbar, suggesting a deep magma storage system in the lower crust at depths of 22–30 km, proximal to the regional Moho (33–35 km). Micro-Fourier Transform Infrared (FTIR) spectrometry was used to determine the structurally bound hydroxyl contents of nominally anhydrous minerals (NAMs) across the three lithologies to reconstruct the volatile evolution of the dike system. Measured structurally bound hydroxyl concentrations in clinopyroxene (80–610 ppm), plagioclase (11–37 ppm), and quartz (2.5–9.5 ppm) indicate moderate to high values. The equilibrium water contents calculated from clinopyroxene range between 0.6 and 4.7 wt.% H₂O. These values are consistent with subduction-related calc-alkaline magmatism, though evidence of re-equilibration with the dacitic melt is observed, aligning with previous quartz-hosted melt inclusion studies. Variations in hydroxyl content between the dacitic host and MMEs record the history of magma mixing. The preservation of high hydroxyl concentrations indicates that the dike did not undergo significant post-emplacement degassing, maintaining high water activity during cooling. This study demonstrates that subvolcanic rocks can effectively preserve primary magmatic water signatures, serving as essential benchmarks for the volatile budgets of post-collisional volcanic systems.

Keywords: magmatic ‘water’, nominally anhydrous minerals, post-collisional, Carpathian–Pannonian region, p–T conditions, FTIR

Introduction

To understand magmatic processes in the lithosphere, the study of rock-forming minerals is of paramount importance. Among these, clinopyroxene in mafic and intermediate-composition magmas is one of the earliest phases to crystallize (Ubide et al. 2019). In understanding the physical conditions of magma evolution, clinopyroxene is an ideal candidate because it is sensitive to pressure, temperature, and water content because

its composition and stability changes with these parameters (e.g., Putirka 2008; Mollo et al. 2013; Ubide & Kamber 2018; Ulmer et al. 2018; Marxer et al. 2022). Studying the structurally bound hydroxyl content of clinopyroxene phenocrysts can provide useful information regarding the water content of the parental melts (Xia et al. 2013; Radu et al. 2023; Kövágó et al. 2025; Patkó et al. 2025).

Furthermore, the structurally bound hydroxyl content of nominally anhydrous minerals (NAMs) can be modified by various magmatic processes, such as: (1) re-equilibration with melts of differing water contents (e.g., Lloyd et al. 2016); (2) diffusional hydrogen loss caused by slow cooling (e.g., Bíró et al. 2017); and (3) oxidation (Skogby & Rossman 1989;

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Stalder & Ludwig 2007; Turner et al. 2017). Looking at the hydroxyl contents considering these processes can provide information about the water content evolution of the magmatic system producing the studied rocks.

In this work, we utilize these features to investigate the Laleaua Albă (“White Tulip”) composite dike (Kovacs & Fülöp 2010), located in the Gutâi Mountains at the eastern margin of the ALCAPA microplate (Săndulescu et al. 1993; Gröger et al. 2008). The studied dike is part of a post-collisional volcanic province (Seghedi et al. 1998; Harangi & Lenkey 2007; Seghedi & Downes 2011; Kovacs et al. 2017). Considering the post-collisional nature of the volcanism of the region it is important to gather information about the volatile budget of rocks as in the post-collisional setting the volcanism is not related to an ongoing active subduction where the water budgets are more clear. Due to its complex evolution – involving magma mixing, mingling, and a distinct cooling history (Kovacs et al. 2010, 2021) – it provides an ideal natural laboratory for utilizing NAMs to investigate these aforementioned phenomena in a natural environment.

Geological background

The Oaş–Gutâi Volcanic Zone (OGVZ) is located at the eastern tip of the ALCAPA microplate, at the contact with the Tisza–Dacia and East European lithospheric plates. It belongs to the Neogene–Quaternary volcanic province of the Carpathian–Pannonian region (CPR), which evolved between 21 and <0.1 Ma (Pécskay et al. 2006; Szakács et al. 2018). The OGVZ consists of two volcanic segments: (i) the Oaş Mountains to the west and (ii) the Gutâi Mountains to the east, the latter being one of the most complex volcanic zones in the CPR (Fig. 1a, c). The E–W striking Bogdan–Dragoş–Vodă fault system (Săndulescu et al. 1993; Gröger et al. 2008), developed south of the Gutâi Mountains, represents the eastward extension of the Mid-Hungarian Fault Zone (Csontos & Nagymarosy 1998) (Fig. 1a).

Volcanic activity in the Gutâi Mountains occurred during the middle Miocene, between 15.4 and 7.0 Ma (Pécskay et al. 2006). Two distinct types of volcanic activity are recognized (Kovacs & Fülöp 2003): (1) felsic (i.e., rhyolitic), caldera-related volcanism, with an onset at ca. 15.4 Ma, partially correlated with the widespread rhyolitic volcanism of the Pannonian Basin (Fülöp 2002, 2003); this activity generated ignimbrites and their resedimented counterparts in the southwestern part of the Gutâi Mountains (Fig. 1c); and (2) intermediate (predominantly andesitic) volcanism developed between 13.4 and 7.0 Ma (Kovacs & Fülöp 2003), covering the entire Gutâi Mountains area. This intermediate activity reached its climactic phase between 11 and 9 Ma and comprises four temporal evolutionary stages (Kovacs et al. 2017).

The first two stages occurred between 13.4 and 9.0 Ma and include several volcanic complexes characterized by temporal, spatial, and compositional affinities. The first volcanic stage developed between 13.4 and 12.1 Ma (Edelstein et al.

1992; Pécskay et al. 1994), primarily in a subaqueous environment, generating andesitic shield volcanoes, lava flows, and extrusive domes in the southeastern and southwestern parts of the OGVZ (Fig. 1c). The most voluminous volcanic activity developed in the central and northern parts of the Gutâi Mountains during the second main volcanic stage (11.6–9.0 Ma), during which predominantly medium-K basaltic andesites, andesites, and dacites were emplaced (Fig. 1c). During this stage, the volcanic pile was accompanied by shallow-level and subvolcanic intrusions (dikes, sills, and small laccoliths) dated between 11.8 and 9.0 Ma (Kovacs et al. 2013), which occur mainly in the southeastern part of the Gutâi Mountains (Fig. 1b, c).

The third volcanic stage is represented by the Laleaua Albă (White Tulip) magmatic complex (LA), consisting of small composite andesitic–dacitic dikes emplaced in the southeastern part of the Gutâi Mountains (8.5–8.0 Ma; Kovacs 2002; Pécskay et al. 2006; Fig. 1b, c). Small intrusive bodies of olivine-bearing basalts (Firiza basalts) developed in the central part of the Gutâi Mountains, marking the final volcanic activity during the fourth stage (8.1–7.0 Ma; Edelstein et al. 1993; Kovacs et al. 2013; Kövágó et al. 2025; Fig. 1b).

Study area and sampling sites

The Laleaua Albă magmatic complex (LA) consists of two small-scale composite dikes which crosscut the volcanoclastic deposits of the second stage of intermediate volcanism. A large outcrop (20 m high, 30 m wide) within a quarry in the main body of one of the two dikes is exposed along the road between Baia Sprie and Sighetu Marmatiei (N 47.689191°, E 23.772387°). The quarry provides a cross-section through the composite dike, revealing two distinct igneous lithologies: a light-colored dacitic core with a tulip-like geometry surrounded by a dark gray andesitic envelope (Fig. 2a). The andesitic envelope exhibits columnar jointing with a polygonal cross-section, which contrasts with the massive texture of the inner dacite.

The dacite displays a macroporphyritic texture, containing large phenocrysts of sanidine (up to 5 cm), plagioclase (up to 3 cm), quartz (up to 1 cm), biotite, amphibole, and pyroxene (Fig. 2b). In contrast, the andesite has an aphanitic to porphyritic texture with sporadic, small-sized phenocrysts of plagioclase, quartz, biotite, amphibole, and pyroxene (Fig. 2c). Abundant mafic microgranular enclaves (MME) of varying sizes (up to 90 cm) occur within the dacite core (Fig. 2d) with decreasing abundance towards the margins, while smaller enclaves are rare within the andesite.

Two main types of MMEs were identified: (1) amphibole + clinopyroxene enclaves (Type 1; Fig. 2d) and (2) clinopyroxene + amphibole enclaves (Type 2; Fig. 2e). A dictytaxitic texture, characterized by elongated, radially arranged prismatic crystals of amphibole and plagioclase, is common in the Type 1 enclaves.

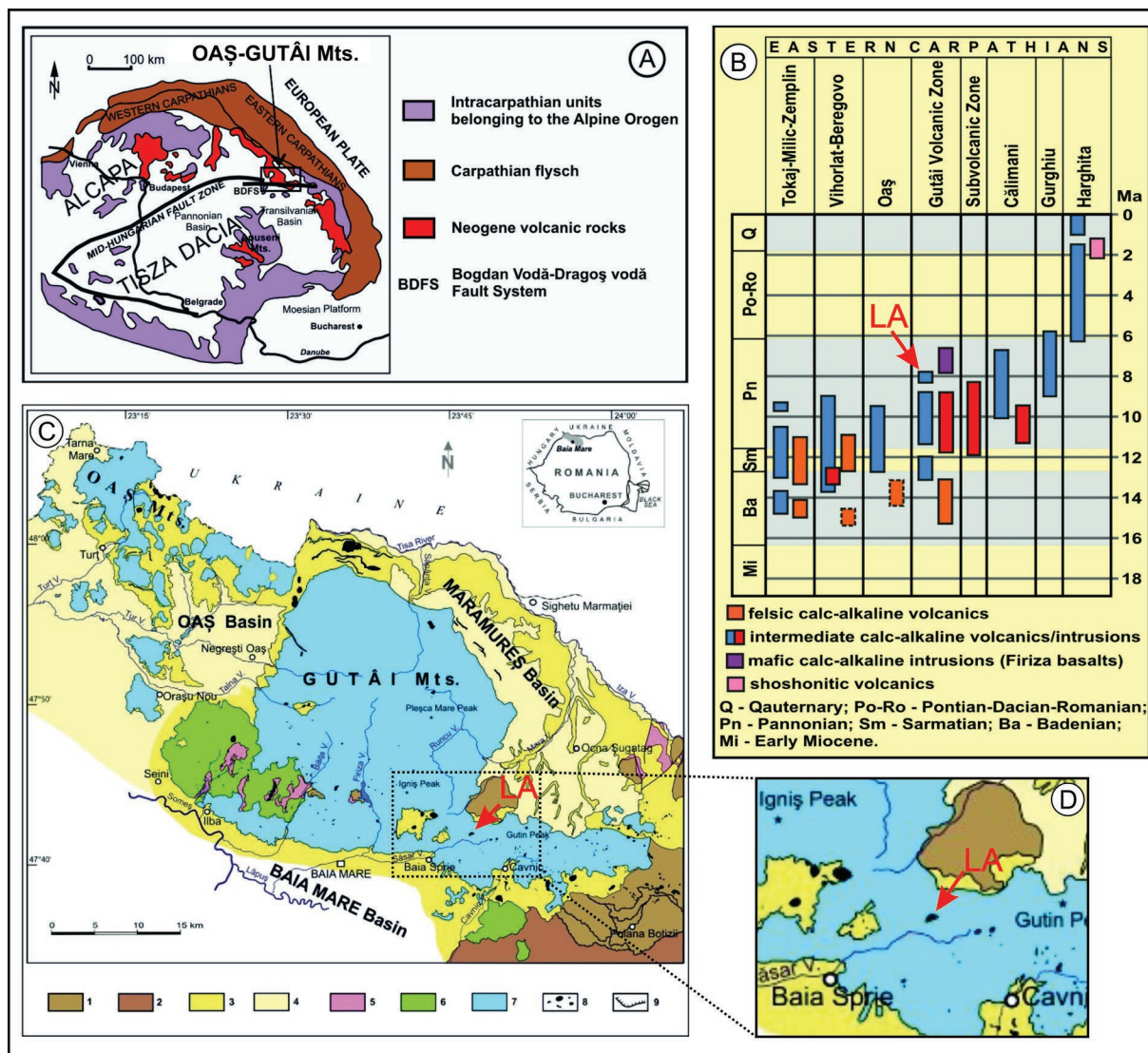


Fig. 1. Location, geology and volcanic rock age distribution of the Oaş-Gutâi Volcanic Zone (OGVZ) and Laleua Albă magmatic complex (LA). (A) Location of the OGVZ within the Carpathian-Pannonian region, (Săndulescu et al. 1993; Gröger et al. 2008); (B) Age distribution of the volcanic products in the Eastern Segment of the Carpathian Volcanic belt with the Laleua Albă magmatic complex (LA) highlighted by the red arrow (after Pécskay et al. 2006; Kovacs et al. 2013). (C) Simplified geological map of the OGVZ with the location of the LA (framed and shown in detail in (D)). Legend: 1 – Paleogene flysch-type sedimentary deposits; 2 – Oligocene-Miocene sedimentary deposits; 3 – Neogene sedimentary deposits; 4 – Quaternary sedimentary deposits; 5 – Badenian felsic volcanoclastic rocks; 6 – First stage intermediate volcanic rocks; 7 – Second stage intermediate volcanic rocks; 8 – intrusive bodies (including LA); 9 – Overthrusts.

Nine samples were collected and analyzed from the Laleua Albă quarry: four from the dacite (GUT 4_3, 4_4, 4_6, and 4_7), one from MME Type 1 (AGUT 14), and four from MME Type 2 (GUT 4_1, AGUT-13, AGUT 17, and AGUT 25). As the outcrop is an inaccessible vertical face, samples were collected from large boulders ranging in size from 1 m up to 10 m at the base of the cliff. The boulders from which the MMEs were collected are located below the central part of the outcrop. This sample gathering introduces an uncertainty about the samples original location within the outcrop, however based on visual observations of the outcrop, the MMEs most often occur in the center part of the outcrop. For each sample,

two 100 µm-thick thin sections were prepared for petrography, along with double-polished sections (~250–300 µm thick) for FTIR analysis.

Sample preparation and analytical methods

Petrography

Petrographic observations were conducted using a Nikon Eclipse LV100 POL polarizing microscope. Microphotography was performed using NIS-Elements software at the Lithosphere

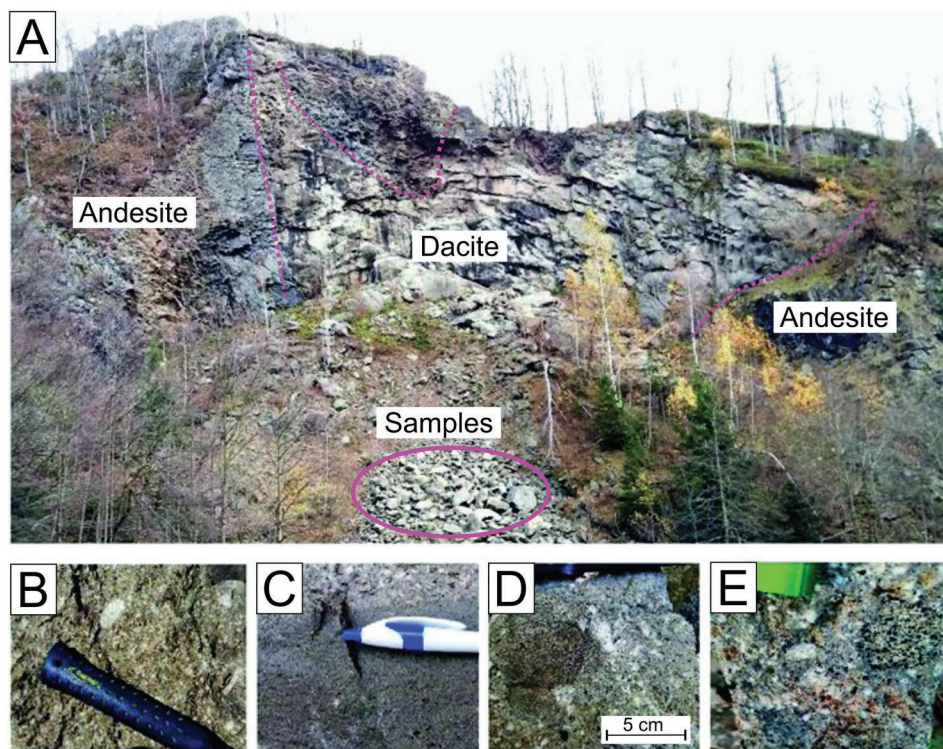


Fig. 2. (A) Outcrop of the main composite dyke of the Laleaua Albă magmatic complex (LA) in the road-side quarry, on the image 'samples' mark the boulders from which the samples were collected. (B) Macroporphritic dacite with large sanidine crystals. (C) Sharp contact between andesite, below, and dacite, above. (D) Amphibole + clinopyroxene microgranular mafic enclave in dacite (MME-type 1). (E) Clinopyroxene + amphibole microgranular mafic enclave in dacite (MME-type 2).

Fluid Research Laboratory (LRG), Institute of Geography and Earth Sciences, Eötvös Loránd University (Budapest). For both petrographic and mineral chemistry studies, 100 μm -thick thin sections were utilized.

Electron probe microanalysis (EPMA)

Major element compositions of clinopyroxenes from ten representative andesites, dacites, and MME (Type 1 and Type 2) enclaves were measured at Queen's University (Kingston, Canada) using a JEOL JXA-8230 electron probe microanalyzer (EPMA). Detailed analytical protocols follow those described by Kovacs et al. (2021).

FTIR and micro-FTIR spectroscopy

The structurally bound hydroxyl contents of nominally anhydrous minerals (NAMs) were determined using micro-Fourier Transform Infrared Spectrometry (micro-FTIR) at the Budapest University of Technology and Economics. The analytical setup consisted of a Spotlight 400 microscope coupled to a Spectrum 400 spectrometer. The measurements were conducted in the MIR range, with SiC source, KBr beamsplitter and MCT detector.

For micro-FTIR analysis, double-polished sections (200–300 μm thick) were prepared and removed from the glass substrates using acetone. To eliminate potential surface-adsorbed water, samples were heated at 90 $^{\circ}\text{C}$ for one hour in the presence of silica gel. The laboratory was air-conditioned to maintain stable temperatures throughout the analytical sessions. To mitigate atmospheric interference, atmospheric

corrections and frequent background measurements were performed. Analytical settings included a 50 $\times$ 50 μm aperture, a spectral resolution of 4 cm^{-1} , 128 scans per measurement, and a spectral range of 400–4000 cm^{-1} .

Data processing and hydroxyl estimation

Recorded spectra were processed using OPUS 7.2 software. Baseline correction was performed using the concave rubber band method (1 iteration, 64 baseline points). Absorbance spectra were first averaged for each individual grain and subsequently averaged for the entire sample. The structurally bound hydroxyl region (3700–3100 cm^{-1}) was integrated using the B-type method, which calculates the area between the spectrum and a line connecting the intersection points of the integration limits.

Structurally bound hydroxyl content was estimated using the Beer–Lambert law, where the concentration of the absorbing molecule is proportional to the integrated absorbance:

$$c_{\text{H}_2\text{O}} = \frac{A^{\text{tot}} \cdot M_A}{\varepsilon \cdot t \cdot \rho} \cdot 100 \quad (1)$$

In Equation (1):

- c : Concentration of the absorbing molecule (wt.%).
- A^{tot} : Total polarized absorbance.
- M_A : Molar weight of water (18.02 g/mol).
- ε : Molar absorption coefficient. Values used include 38,300 $\pm$ 1700 $\text{L}/(\text{mol H}_2\text{O} \cdot \text{cm}^2)$ for augite (Bell et al. 1995); 202,600 $\pm$ 20,260 $\text{L}/(\text{mol H}_2\text{O} \cdot \text{cm}^2)$ for plagioclase (Mosenfelder et al. 2015); and 94,000 $\pm$ 20,000 $\text{L}/(\text{mol H}_2\text{O} \cdot \text{cm}^2)$ for quartz (Thomas et al. 2009).

- **t**: Sample thickness (cm), with an uncertainty of $\pm 1 \mu\text{m}$.
- **ρ** : Mineral density (g/L). Values used include 3256 g/L for clinopyroxene (Bell et al. 1995); 3680 g/L for plagioclase (Libowitzky & Rossman 1997); and 2650 g/L for quartz (Thomas et al. 2009).

Structurally bound hydroxyl content is expressed as H_2O equivalent in ppm by weight. Total polarized absorbance (A^{tot}) was estimated from unpolarized radiation following the methods of Kovács et al. (2008) and Sambridge et al. (2008), where A^{tot} is three times the average integrated unpolarized absorbance. This method is valid when the maximum linear unpolarized absorbance is below 0.15 absorbance units, a condition met by all studied samples. For each sample, at least five (and ideally more than ten) unoriented grains were analyzed to ensure statistical accuracy.

The cumulative uncertainty remains below 10 % when at least five unoriented crystals are available (Patkó et al. 2019). Error propagation followed the method described by Patkó et al. (2019), accounting for uncertainties in the extinction coefficient, density, thickness, and total polarized absorbance. Xia et al. (2013) demonstrated that the uncertainty in the structurally bound hydroxyl content is less than 30 % even if only one crystallographic orientation is available. For samples where only one clinopyroxene grain was available, the calculated error is 10.5 %. To assess the homogeneity of hydroxyl distribution, transect measurements were performed across selected grains.

Clinopyroxene selection criteria

To accurately determine the water content of the primitive parent melt, specific selection criteria were applied:

- **Crystallization Stage**: Crystals representing the earliest crystallization stage in equilibrium with the parent melt were prioritized (e.g., cores of early phenocrysts or glomerocrysts).
- **Zoning**: In zoned crystals, cores were preferred as they are more likely to preserve original hydroxyl concentrations.
- **Mineral chemistry**: Clinopyroxenes with $\text{Mg}\# > 75$ (ideally > 80) were selected, consistent with established protocols (Xia et al. 2013; Liu et al. 2016).
- **Physical Quality**: Analyzed grains were required to be free of inclusions, secondary alterations, and exsolution lamellae.

Results

Petrography and mineralogy

The investigated lithologies include andesite, dacite, and two types of mafic microgranular enclaves (MME Type 1 and Type 2). The andesite is composed of plagioclase, quartz, biotite, amphibole, and clinopyroxene. The dacite contains K-feldspar, plagioclase, amphibole, quartz, biotite, and clinopyroxene. The MMEs consist of plagioclase, clinopyroxene, and amphibole; specifically, Type 1 is amphibole-dominated,

while Type 2 is clinopyroxene-dominated. The characteristics of these minerals are detailed below.

K-feldspar (sanidine) is the most prominent mineral in the macroporphyrific dacite. It occurs exclusively in this lithology as large phenocrysts (up to several centimeters) exhibiting typical Carlsbad twinning. These sanidine crystals contain inclusions of plagioclase, biotite, and, less frequently, amphibole (Kovács & Fülöp 2010).

Plagioclase crystals occur in at least two distinct generations. Large ($> 1 \text{ cm}$), euhedral, twinned phenocrysts with common overgrowths are restricted to the dacite. Conversely, smaller plagioclase crystals, which predominantly occur in the andesites, often exhibit oscillatory zoning and sieve-textured or “dusty” cores (Kovács & Fülöp 2010).

Quartz phenocrysts are larger and more abundant in the dacite than in the andesite. Large dacitic quartz phenocrysts are frequently subrounded, embayed, and corroded. In the andesites, quartz phenocrysts are often surrounded by clinopyroxene coronas.

Biotite occurs as large phenocrysts (up to 0.8 cm) and is more abundant in the dacites compared to the andesites.

Amphibole phenocrysts in the dacites are more numerous and larger (average 1.5 mm) than those in the andesites (average 0.5 mm). These amphiboles are interpreted as xenocrysts in both dacites and andesites.

Pyroxenes are represented almost exclusively by clinopyroxene. These occur predominantly as clusters in the andesites and more rarely as individual crystals (Fig. 3). The clinopyroxenes across the three rock types are remarkably similar and are interpreted as xenocrysts within the dacites and andesites.

Mineral chemistry

Clinopyroxene

Clinopyroxenes from the andesites and dacites (xenocrysts) and from the MMEs are classified as diopside and augite according to the IMA classification (Morimoto et al. 1988; Fig. 4). They exhibit a narrow compositional range: $\text{Wo}_{38.7-48.1} \text{En}_{36.8-48.7} \text{Fs}_{7.1-18.8}$.

The clinopyroxenes across both rock types and both MME types generally display similar major element compositions. SiO_2 contents range from 45 to 53 wt.% (mostly 48–52 wt.%), while Al_2O_3 varies between 1.5 and 8.7 wt.%, with most data clustering between 2.0 and 6.0 wt.%. Na_2O ranges from 0.10 to 0.30 wt.% (mostly 0.12–0.25 wt.%), and CaO contents are largely restricted to a narrow interval of 20–23 wt.%. MgO values vary from 11.8 to 17.8 wt.%, and FeO ranges from 3.5 to 11.8 wt.% (mostly 4–10 wt.%). TiO_2 contents range between 0.10 and 1.50 wt.% (mostly 0.25–1.25 wt.%), and Cr_2O_3 values typically range from 0.0 to 0.7 wt.%.

Al_2O_3 and TiO_2 show strong negative correlations with SiO_2 , whereas MgO correlates positively (Fig. 5). Although the clinopyroxenes are generally similar, those from the clinopyroxene+amphibole MME (Type 2) enclaves plot at the higher

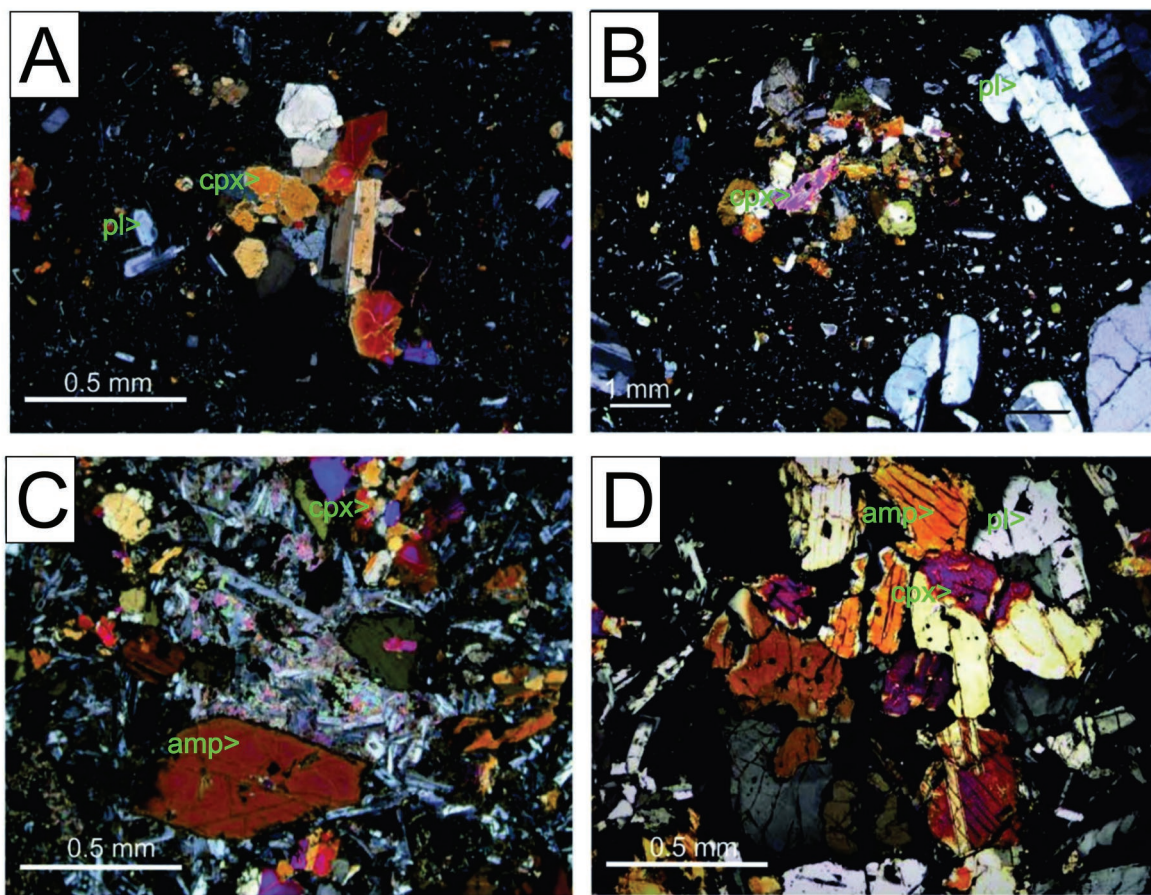


Fig. 3. Clinopyroxenes in andesites (A), dacites (B), amphibole+clinopyroxene mafic microgranular enclaves MME-type 1 (C) and clinopyroxene+amphibole MME-type 2 (D). Abbreviations: cpx=clinopyroxene; pl=plagioclase; amp=amphibole.

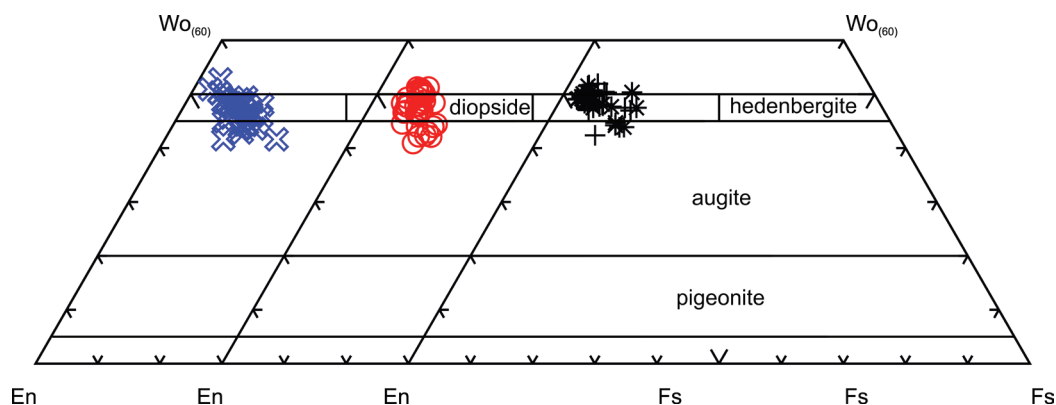


Fig. 4. Distribution of the clinopyroxenes from the Laleaua Albă magmatic rocks in the classification diagram of Morimoto et al. (1988). Symbols: blue cross – clinopyroxenes from andesites; red circle – clinopyroxenes from dacites; black cross – clinopyroxenes from amphibole+clinopyroxene MME (type-1); black asterisk – clinopyroxenes from clinopyroxene+amphibole MME (type-2).

end of the MgO vs. SiO₂ variation field and at the lower end of the Al₂O₃ and TiO₂ vs. SiO₂ diagrams.

Mg# values range from 67 to 89 (mostly 73–85). Specifically, clinopyroxenes from the andesites range from 67 to 85 (mostly 72–80). Similar ranges are observed in the dacites (72–86) and MME Type 1 (72–86). The clinopyroxenes from MME

Type 2 enclaves range from 67 to 89, with the majority exceeding 80.

FeO and Fs display strong negative correlations with Mg#, while En and CaO show positive correlations (Fig. 6). A general negative correlation is observed between TiO₂ and Mg#. Conversely, Cr₂O₃ and Mg# show a slight positive correlation

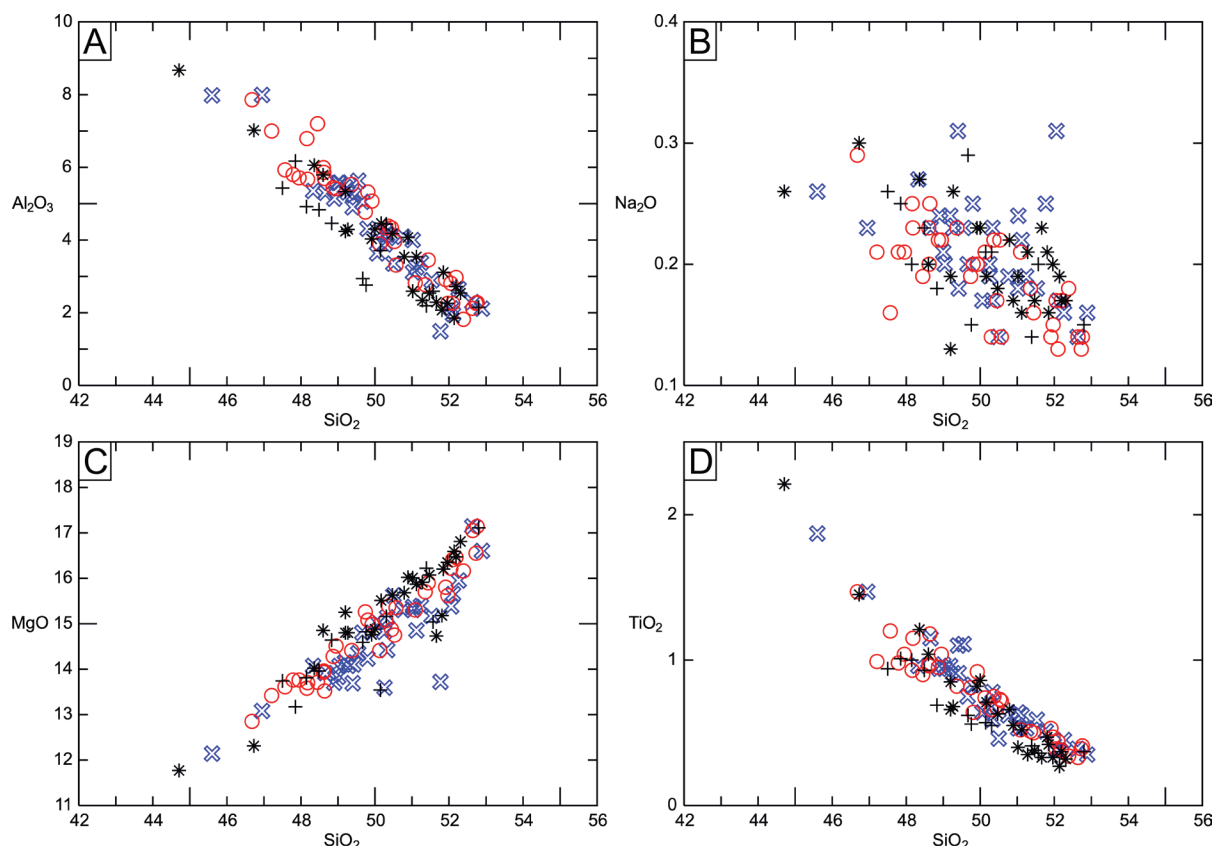


Fig. 5. Major elements plotted against SiO₂ of the clinopyroxenes from andesites, dacites and MME (symbols as in Fig. 4).

at higher Mg# values, particularly for clinopyroxenes from the MME Type 2 enclaves (Fig. 6). Based on these chemical signatures, clinopyroxenes from MME Type 2 are characterized by the highest Mg#, CaO, and Cr₂O₃, and the lowest FeO contents.

Amphibole

Amphiboles in the dacites, andesites, and mafic enclaves are exclusively high-Al and high-Mg# varieties, classified as magnesio-hastingsite, pargasite, and sadanagaite (Kovacs et al. 2021).

Plagioclase

Plagioclase in the dacite can be divided into two groups: (1) large crystals (>1 cm) that are strongly oscillatory zoned with low anorthite content (An₂₈₋₄₃); and (2) crystals with more calcic cores (An₆₅₋₇₅) interpreted as antecrysts (Kovacs et al. 2021). This second type, which occasionally exhibits sieve textures, is also present in the andesites and MMEs.

Clinopyroxene geothermobarometry

The pressure (P) and temperature (T) of clinopyroxene crystallization were calculated using the models proposed by

Putirka (2008). Equilibrium between clinopyroxene and the host liquid was assessed using the Fe–Mg exchange coefficient ($K_D^{cpx-liq}$), with a target value of 0.27 ± 0.03 (Putirka 2008). Additionally, following the recommendations of Neave & Putirka (2017), the Diopside–Hedenbergite (DiHd) component equilibrium test was applied, requiring predicted and observed values to be within a 20 % margin (Fig. 7).

Pressures were calculated using Equation 31 (Standard Error of Estimate, SEE = ± 2.9 kbar) and temperatures using Equation 33 (SEE = ± 45 °C) from Putirka (2008) (see Supplementary Data S1 and S2 for detailed calculations).

The calculated P values range from 4.0 to 10.3 kbar. Only five values exceed 9 kbar, while the vast majority fall within a narrow 3.0 kbar interval between 5.5 and 8.5 kbar (Fig. 8a). Calculated temperatures vary from 1040 to 1125 °C, with most data points clustered within a 50 °C range (Fig. 8a). As shown in the P–T diagram, the crystallization conditions for clinopyroxenes from andesites, dacites, and MMEs overlap significantly, suggesting they originated from a common magmatic environment.

Based on the dominant crystallization pressure range (5.5–8.5 kbar) and an average crustal density for the Gutâi Volcanic Zone of 2700 kg/m³ (Kovacs et al. 2021), it is inferred that the clinopyroxenes from the Laleaua Albă magmatic rocks crystallized within a magma storage system situated in the lower crust at depths of 20–33 km (Fig. 8b).

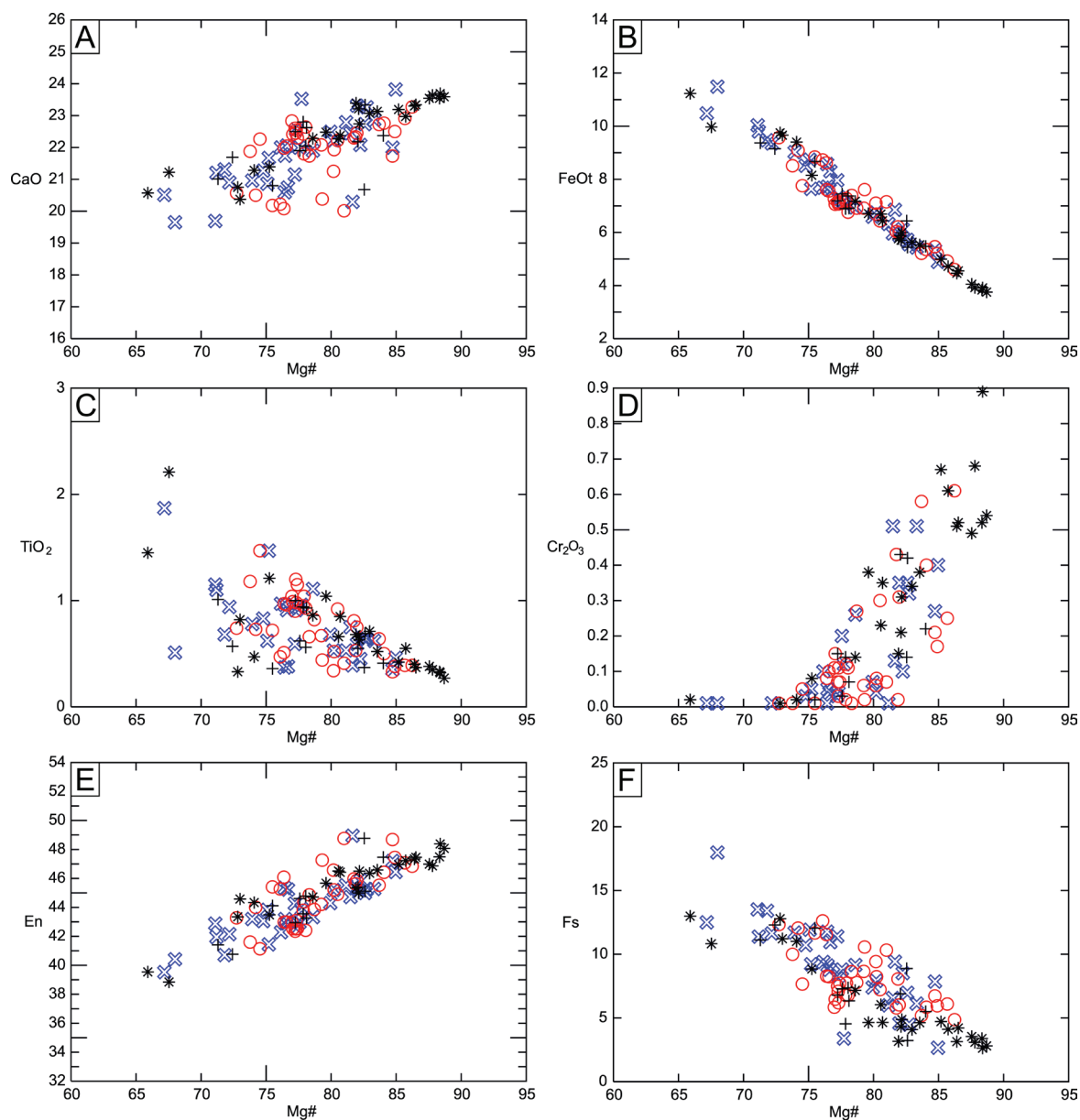


Fig. 6. Major elements vs. Mg# values for the clinopyroxenes from andesites, dacites and MME (symbols as in Fig. 4).

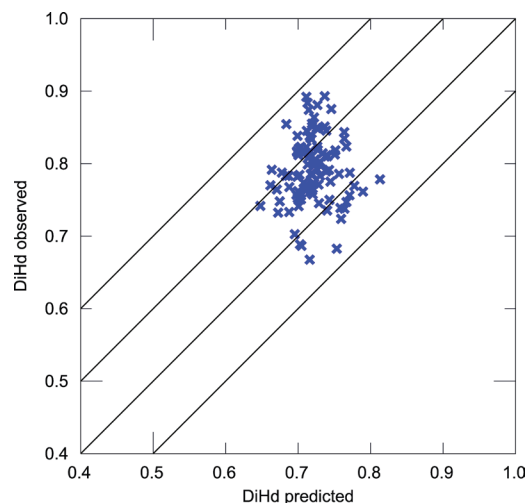
Fig. 7. Mineral DiHd equilibrium tests for clinopyroxenes from the Laleua Albă magmatic rocks.

FTIR study

The structurally bound hydroxyl contents of clinopyroxene phenocrysts from nine samples of dacite and MMEs were determined using FTIR spectroscopy (Table 1). Representative unpolarized average infrared spectra, normalized to a thickness of 1 cm, are illustrated in Figure 9.

Clinopyroxene spectral characteristics

Three major absorption bands were identified in the structurally bound hydroxyl region of the investigated clinopyro-



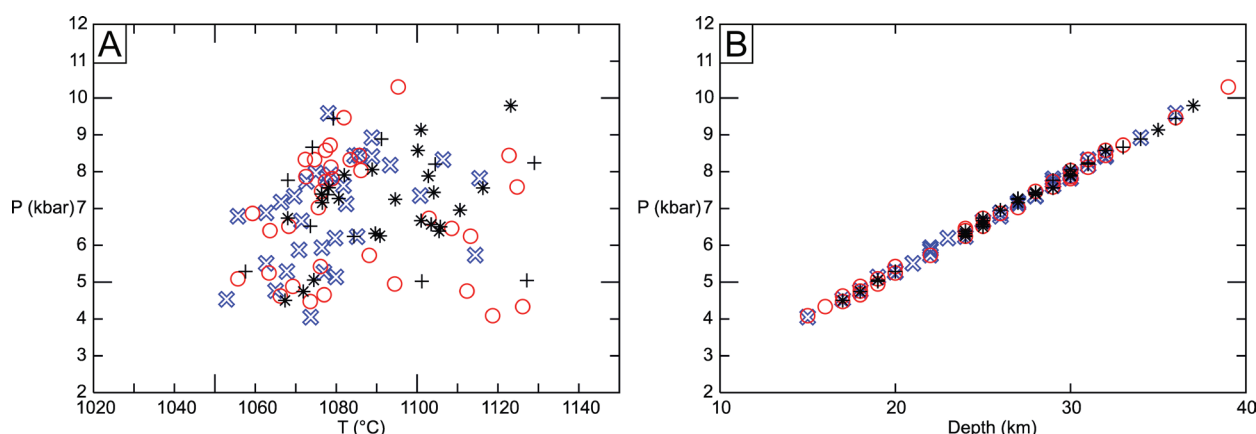


Fig. 8. Pressure vs. temperature (A) and pressure vs. depth (B) for the clinopyroxenes from the Laleaua Albă magmatic rocks (symbols as in Fig. 4).

Table 1: Information about the samples related to the clinopyroxene FTIR studies.

Sample	GUT 4_1	GUT 4_3	GUT 4_4	GUT 4_6	GUT 4_7	AGUT 13	AGUT 14	AGUT 17	AGUT 25
Number of analyzed grains	7	2	2	1	5	5	2	5	7
Thickness (μm)	245	250	245	225	260	205	195	195	200
H ₂ O (ppm wt.)	80	155	370	530	615	375	405	240	130
Relative uncertainty (10 %)	5	13.2	31	56	42	25	34	16	8
Rock type	MME (type 2)	dacite	dacite	dacite	dacite	MME (type 2)	MME (type 1)	MME (type 2)	MME (type 2)

xene crystals: approximately 3630, 3520, and 3470 cm^{-1} . Additional weak bands at approximately 3350 and 3250 cm^{-1} were also observed in some samples. The relative intensities of these absorption bands vary across the samples (Fig. 9):

- **Sample GUT 4_7:** Exhibits bands at 3630, 3520, and 3470 cm^{-1} , with the 3520 cm^{-1} band showing the highest absorbance.
- **Sample GUT 4_4:** Shows bands at 3630, 3520, and 3470 cm^{-1} , with intensity decreasing toward lower wavenumbers.
- **Sample GUT 4_6:** The 3630 cm^{-1} band is the least intense, while the 3520 and 3470 cm^{-1} bands are significant. A broad band is also visible between 3300 and 3200 cm^{-1} .
- **Sample AGUT 13:** The most intense band is at 3630 cm^{-1} , followed by 3520 cm^{-1} and 3470 cm^{-1} .

Samples AGUT 14, 17, and 25: The intensity follows a decreasing order from 3520 cm^{-1} to 3470 cm^{-1} , and finally 3630 cm^{-1} .

Hydroxyl concentrations

The calculated structurally bound hydroxyl contents for the analyzed samples are as follows:

- **GUT 4_1:** 80 $\pm$ 5 ppm
- **GUT 4_3:** 160 $\pm$ 13 ppm
- **GUT 4_4:** 370 $\pm$ 31 ppm
- **GUT 4_6:** 530 $\pm$ 56 ppm
- **GUT 4_7:** 610 $\pm$ 42 ppm

- **AGUT 13:** 370 $\pm$ 25 ppm
- **AGUT 14:** 400 $\pm$ 34 ppm
- **AGUT 17:** 240 $\pm$ 16 ppm
- **AGUT 25:** 130 $\pm$ 8 ppm (Table 1)

Quartz

In quartz, infrared absorption bands were observed at 3440, 3378, 3310, and 3200 cm^{-1} , with the 3378 cm^{-1} band being the most prominent. Sample GUT 4_3 exhibited the highest absorption intensities, followed by GUT 4_4, 4_5, and 4_6. Narrow, comb-like bands related to atmospheric water vapor (moisture) were observed above 3500 cm^{-1} ; however, these did not significantly overlap with the structurally bound hydroxyl region of the mineral.

The calculated structurally bound hydroxyl contents for quartz are as follows:

- **GUT 4_3:** 9.5 $\pm$ 0.95 ppm
- **GUT 4_4:** 4.6 $\pm$ 0.46 ppm
- **GUT 4_5:** 3.0 $\pm$ 0.3 ppm
- **GUT 4_6:** 2.5 $\pm$ 0.25 ppm

Plagioclase

Plagioclase spectra revealed three broad absorption bands centered at approximately 3600, 3400, and 3200 cm^{-1} . For samples GUT 4_1, 3, 4, 5, and 7, the most prominent band

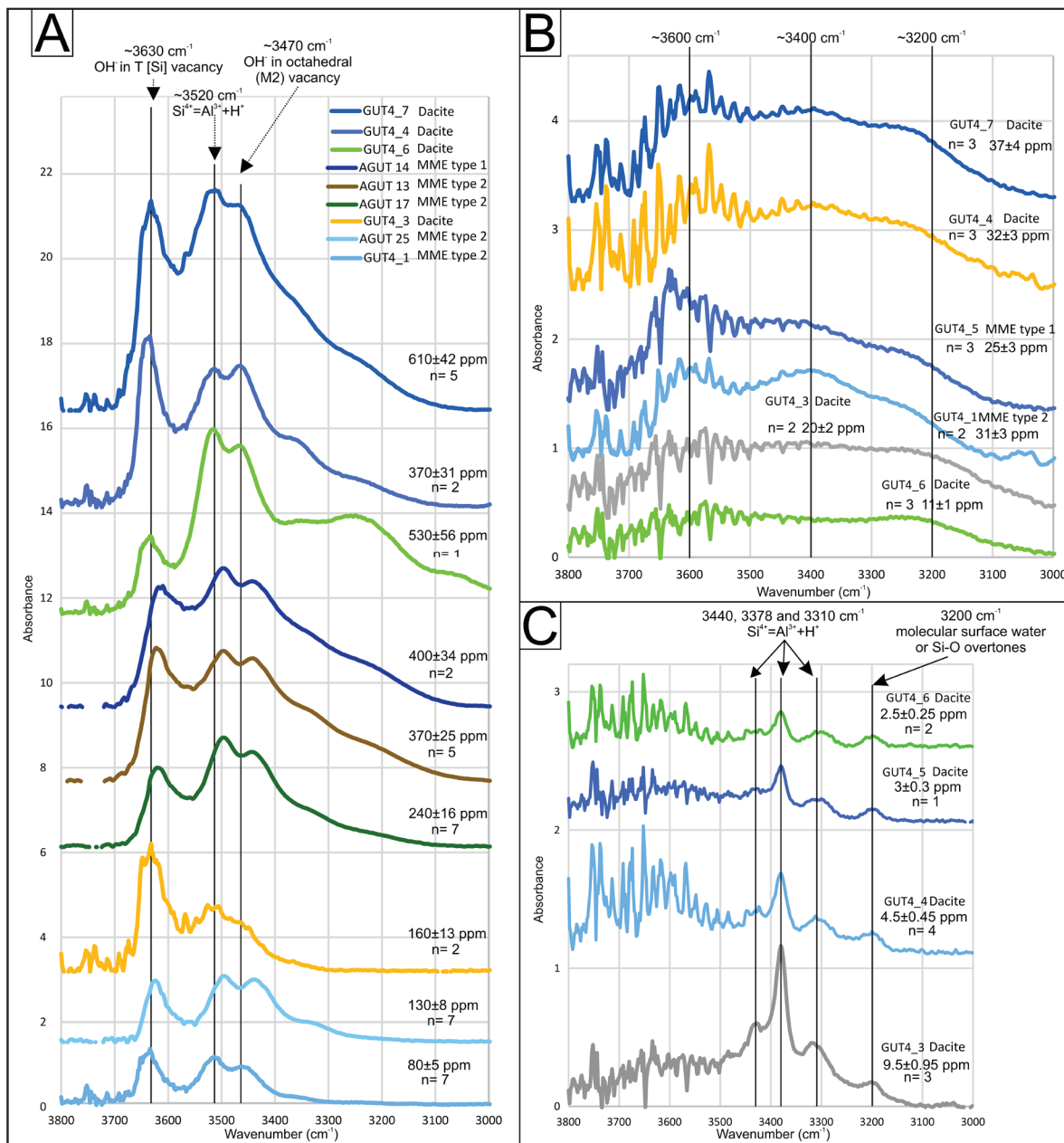


Fig. 9. Average FTIR spectra of clinopyroxene (A), plagioclase (B) and quartz (C) from each sample normalized to 1 cm, showing the observed absorption bands, noted its substitution, based on the literature for clinopyroxene (Smyth et al. 1991; Bromiley et al. 2004; Koch-Müller et al. 2004; Stalder & Ludwig 2007), for plagioclase (Johnson & Rossman 2004) and for quartz (Kats 1962), also presented the structural hydroxyl content, its error, and the rock type of the samples.

is located at ~3400 cm⁻¹. The ~3600 cm⁻¹ band frequently exhibited spectral interference from atmospheric water. The intensity of the 3200 cm⁻¹ band was consistently lower than the other two major bands. In sample GUT 4_6, the 3600 and 3200 cm⁻¹ bands showed similar intensities, while the 3400 cm⁻¹ band was not clearly distinguishable.

The calculated structurally bound hydroxyl contents for plagioclase are:

- GUT 4_1: 30±3 ppm
- GUT 4_3: 20±2 ppm

- GUT 4_4: 32±3.2 ppm
- GUT 4_6: 11±1 ppm
- GUT 4_7: 37±3.7 ppm

Water content of the parent melts in equilibrium with clinopyroxene

To estimate the water content of the melts in equilibrium with the studied clinopyroxenes, we employed the composition-dependent partition coefficient proposed by O'Leary et

al. (2010), following the methodologies outlined in Kovács et al. (2020) and Kővágó et al. (2025). The resulting water contents were adjusted using fractionation factors of 0 %, 5 %, 10 %, 15 %, 20 %, and 25 % to account for the enrichment of water in the residual melt during crystal fractionation.

The calculated water contents (assuming a 10 % uncertainty for the FTIR measurements and a 20 % fractionation correction) range between 0.98 and 4.72 wt.% H₂O for the melt in equilibrium with dacitic clinopyroxenes, 3.06–3.75 wt.% H₂O for MME Type 1, and 0.57–3.21 wt.% H₂O for MME Type 2 enclaves (Fig. 10). The water content range of the parental melts in which the Laleaua Albă clinopyroxenes crystallized is compared to other studies in Figure 10.

Discussion

Clinopyroxene crystallization

The clinopyroxenes from the andesite, dacite, and MMEs of the Laleaua Albă magmatic complex originate from the same deep magmatic source (Kovács et al. 2021). The major element compositions of these clinopyroxenes fall within a narrow range and exhibit overlapping fields in the variation diagrams (Fig. 6).

Furthermore, thermobarometric calculations on the clinopyroxene phenocrysts yield consistent results, with temperatures of 1040–1125 °C and pressures of 5.5–8.5 kbar. These values correspond to crystallization depths of 20–33 km (Kovács et al. 2021), pointing toward a common upper mantle source and subsequent magmatic evolution within the lower crust (Fig. 8). These calculated depths align closely with regional Moho depth determinations reported in the literature (Săndulescu et al. 1993; Bielik et al. 2018; Kalmár et al. 2019).

Water content of NAMs and magmatic processes

Substitution mechanisms

The various absorption bands observed in the FTIR spectra of the NAMs are attributed to specific structural substitutions:

- **Clinopyroxene:** The band at $\sim 3630\text{ cm}^{-1}$ is linked to OH⁻ in tetrahedral site [Si] vacancies or coupled $\text{Na}^+ + \text{H}^+ \leftrightarrow \text{M}$ substitutions in the octahedral site (Bromiley et al. 2004; Stalder & Ludwig 2007). The band at $\sim 3520\text{ cm}^{-1}$ relates to $\text{Al}^{3+} + \text{H}^+ \leftrightarrow \text{Si}^{4+}$ substitution (Koch-Müller et al. 2004), and the band at $\sim 3470\text{ cm}^{-1}$ is attributed to OH⁻ in octahedral (M2) vacancies (Smyth et al. 1991).
- **Quartz:** The 3378, 3440, and 3310 cm^{-1} bands relate to $\text{Al}^{3+} + \text{H}^+ \leftrightarrow \text{Si}^{4+}$ coupled substitution (Kats 1962).
- **Plagioclase:** The bands reflect structurally bound Type IIb OH (Johnson & Rossman 2004).

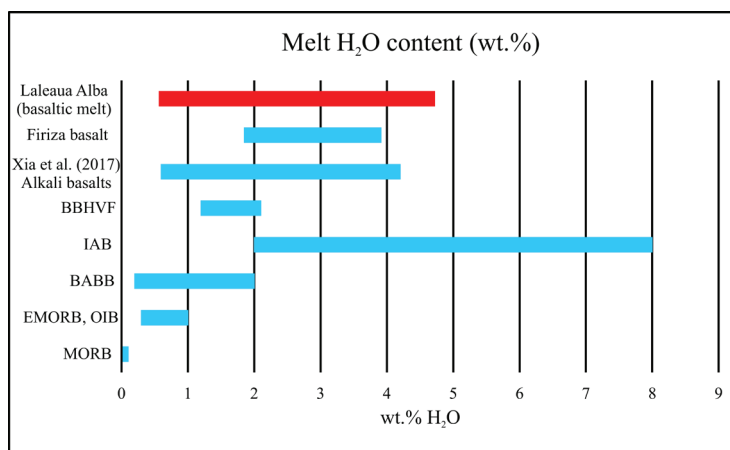


Fig. 10. The calculated melt water content for the basaltic melt from which the clinopyroxenes crystallized at depths of 20–32 km based on the thermobarometric calculations, compared to the values reported by previous studies (Dixon et al. 2004; Xia et al. 2017; Kovács et al. 2020; Kővágó et al. 2025).

Comparison with global data

The structurally bound hydroxyl contents of the Laleaua Albă (LA) clinopyroxenes were compared to values from previous studies (Fig. 11). The maximum values measured in LA clinopyroxenes are notably higher than those reported from natural alkali basalts and mantle xenoliths worldwide (Liu et al. 2015; Kovács et al. 2016; Patkó et al. 2019). While the concentrations reported by Weis et al. (2015) and Radu et al. (2023) for natural clinopyroxene phenocrysts prior to rehydration are generally lower, their experimental rehydration results overlap with the LA values. Furthermore, while some water concentrations reported by Wade et al. (2008) are lower, the majority are consistent with the LA data. Other reported concentrations in the literature fall within a similar range (Nazzareni et al. 2008, 2011; Okumura 2011; Lloyd et al. 2016; Turner et al. 2017). Notably, the structurally bound hydroxyl contents of the Laleaua Albă clinopyroxenes span a wide range, and their maximum values exceed the highest values reported globally.

The structurally bound hydroxyl content of the Laleaua Albă quartz is compared to literature values in Figure 11. The LA values overlap with the bulk of previously reported data for various environments, including siliciclastic sediments, eclogite, gneiss, quartzite, rhyolite, hydrothermal systems, and granite (e.g., Yurimoto et al. 1989; Müller & Koch-Müller 2009; Stalder & Neuser 2013; Stalder 2014; Biró et al. 2016, 2017; Stalder et al. 2017, 2019; Potrafke et al. 2020). While the LA results are consistent with typical ‘common’ quartz and rock crystal ranges, some literature values for pegmatites and hydrothermal quartz are notably higher, whereas some granitic and rhyolitic samples report lower concentrations.

The structurally bound hydroxyl contents of plagioclase in this study are generally lower than most literature values.

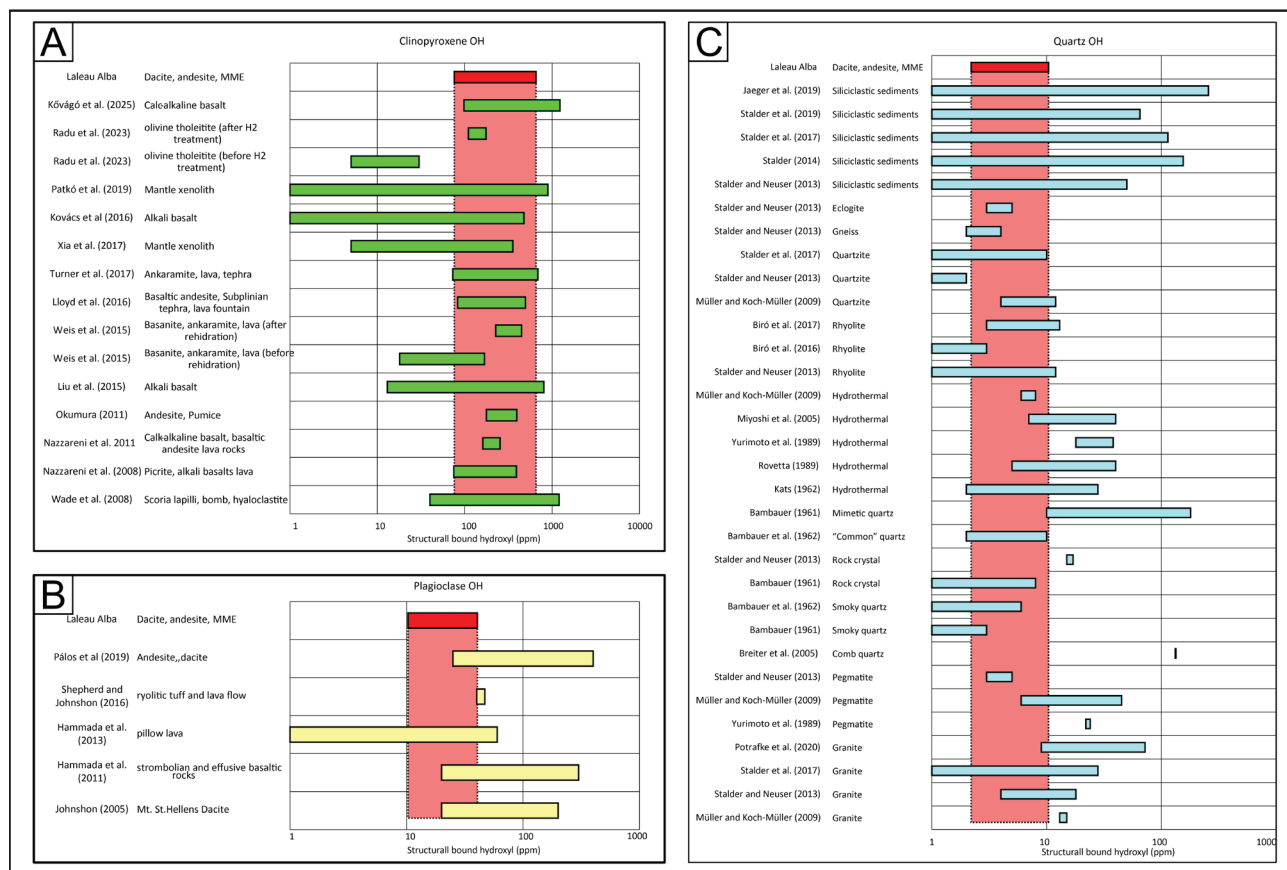


Fig. 11. The measured structural hydroxyl contents in the Laleau Albia clinopyroxenes (**A**), plagioclases (**B**) and quartzes (**C**). The clinopyroxene results are compared to the values reported by previous studies (Nazzareni et al. 2008, 2011; Wade et al. 2008; Okumura 2011; Liu et al. 2015; Weis et al. 2015; Kovács et al. 2016; Lloyd et al. 2016; Turner et al. 2017; Xia et al. 2017; Patkó et al. 2019; Radu et al. 2023; Kővágó et al. 2025). The plagioclase results are compared to the values reported by previous studies (Johnson 2005; Hamada et al. 2011, 2013; Shepherd & Johnson 2016; Pálos et al. 2019). The quartz results are compared to the values reported by previous studies (Bambauer 1961; Bambauer et al. 1962; Kats 1962; Rovetta 1989; Yurimoto et al. 1989; Breiter et al. 2005; Miyoshi et al. 2005; Müller & Koch-Müller 2009; Stalder & Neuser 2013; Stalder 2014; Biró et al. 2016, 2017; Stalder et al. 2017, 2019; Jaeger et al. 2019; Potrafke et al. 2020).

However, they overlap with the lower end of reported ranges for volcanic and plutonic plagioclase (e.g., Johnson 2005; Hamada et al. 2011; Shepherd & Johnson 2016; Pálos et al. 2019) and remain higher than those reported by Hamada et al. (2013) (Fig. 11).

Comparative hydroxyl variations and evolutionary paths

FTIR spectra of clinopyroxenes from the MMEs are uniform, whereas those in the dacite are significantly more diverse (Fig. 9). As discussed previously the different bands on the FTIR spectra and their intensities mean different substitution where the intensity proportional with the concentration of the given substitution which depends on the chemistry of the melt in equilibrium with them. The dacite-hosted clinopyroxenes (140–650 ppm) show moderately higher hydroxyl contents than those from the MMEs (80–440 ppm), though their ranges overlap (Fig. 12). The structurally bound hydroxyl content of the minerals related to the water content of the melt

from which the minerals crystallized or re-equilibrated with. Based on these informations the two groups of clinopyroxenes either crystallized from or equilibrated with different melts. Given their shared deep-seated origin, these differences suggest that the MMEs and dacite followed divergent evolutionary paths through the lithosphere.

Thermobarometric data indicate these minerals crystallized at depths of 20–33 km (5.5–8.5 kbar) under similar conditions, likely with an initial water content of ~4 wt.% (Fig. 10). Consequently, the observed discrepancies must have occurred during later magmatic stages. A plausible model involves deep-seated basaltic melt being supplied to a shallower reservoir (4–8 km depth, ~800 °C) containing high-silica rhyolitic melts (5–6 wt.% H₂O; Liu et al. 2005). The dacitic clinopyroxenes likely represent multiple recharge events, while the MMEs were likely incorporated during the final recharge event, a theory supported by their large size, integrity and higher abundance in the inner parts of the dacitic core.

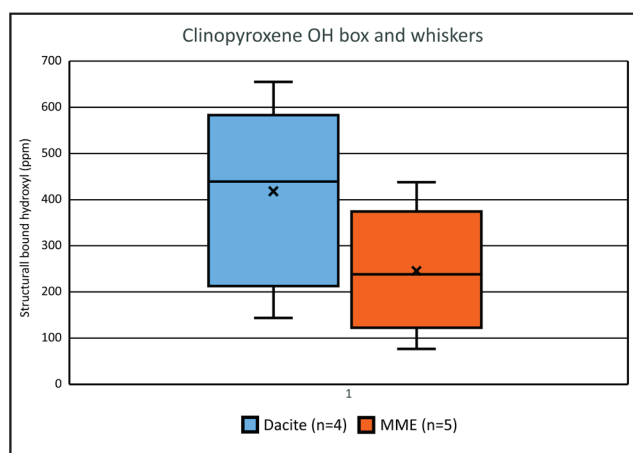


Fig. 12. Box and whiskers plot showing the structural hydroxyl contents of clinopyroxenes from the dacite and the MME's. It can be observed that the samples from the dacite cover a wider field and have higher values than the ones from the MME's.

Post-emplacement processes and diffusion

Post-emplacement cooling can cause water loss if crystals spend prolonged time at high temperatures in low water-activity environments (Biró et al. 2017). Because MMEs are more likely from the core of the dike based on their occurrence inside the dike and the characteristics of the sampling, they should theoretically experience longer cooling times and lower hydroxyl contents than the dacite located closer to the country rock (Fig. 12).

However, diffusional hydrogen loss is likely not the dominant factor here. High hydroxyl contents persist in clinopyroxenes from both rock types. Furthermore, quartz with much higher H^+ diffusion rates (Farver 2010), still retain structurally bound hydroxyl (2.2–10.5 ppm) (Fig. 11). This preservation suggests either very rapid cooling or a lack of complete degassing in the dike, maintaining a high water activity during the cooling phase.

Fractional crystallization and oxidation

During fractional crystallization, water behaves incompatibly (partition coefficients for Cpx and Pl are <1 ; Aubaud et al. 2004), causing it to enrich in the residual melt. If no degassing occurs, clinopyroxene can re-equilibrate with this increasingly hydrous melt.

Oxidation of Fe^{2+} to Fe^{3+} can also decrease hydroxyl content according to the reaction: $Fe^{3+} + O^{2-} + 0.5 H_2 = Fe^{2+} + OH^-$ (Skogby & Rossman 1989). While ascending through the more oxidizing crust, primitive clinopyroxenes could undergo this process. Although no petrographic signs of oxidation are visible on the clinopyroxenes (e.g. reddish discoloration), the cation calculations conducted on the clinopyroxenes show that the measured crystals have Fe^{3+} lower than Fe^{2+} and infrared bands related to Fe^{2+} (3470 cm^{-1}) are present, however this

mechanism cannot be entirely ruled out without specific analytical data (e.g., Mössbauer spectroscopy or XANES) on the iron oxidation state.

Summarizing the effects on the structurally bound hydroxyl content

The most likely processes influencing the structurally bound hydroxyl content in the Laleaua Albă samples are:

- **Partial re-equilibration** with the hydrous dacitic melt during ascent/mixing.
- **Minor diffusional hydrogen loss** during post-emplacement cooling.

Contrary to studies of ignimbrites where minerals often lose their hydroxyl content (e.g., Biró et al. 2016; Hencz et al. 2021), the Laleaua Albă NAMs (Clinopyroxene: 80–610 ppm, Plagioclase: 10–40 ppm, Quartz: 2.2–10.5 ppm) suggest that water activity remained high during cooling due to a lack of post-emplacement degassing. This establishes that subvolcanic bodies like the Laleaua Albă complex can successfully preserve original magmatic water signatures.

Water content of the parental melts in equilibrium with clinopyroxene

The calculated water content of the clinopyroxene samples provides insight into the volatile budget of the parental melts that produced the phenocrysts found in the dacite and the two types of MMEs. However, as previously discussed, the structurally bound hydroxyl contents likely underwent modifications relative to their primary magmatic values.

Re-equilibration and cooling effects

Clinopyroxenes within the dacite likely equilibrated with the host dacitic melt to some extent, resulting in higher calculated water contents (0.98–4.72 wt.%) compared to those from the MMEs (0.57–3.75 wt.%). The lower values in the MMEs are likely a result of their more central location within the dike, which potentially led to slower cooling rates and a higher probability for diffusional hydrogen loss.

Despite these modifications, both ranges overlap significantly with globally measured water contents in basaltic magmas (Fig. 10). Specifically, they align with the ranges for Back-Arc Basin Basalts (BABB: 0.2–2 wt.%) and Island Arc Basalts (IAB: 2–8 wt.%) reported by Dixon et al. (2004), as well as values reported in regional studies (Kovács et al. 2020: 1.2–2.1 wt.%; Xia et al. 2017: 0.6–4.2 wt.%; Patkó et al. 2025: 1.5–2.08 wt.%; Kővágyó et al. 2025: 1.85–3.91 wt.%).

Comparison with melt inclusion data

Our findings are further supported by Naumov et al. (2014), who studied water contents in melt inclusions within quartz phenocrysts from the Laleaua Albă dacite. Using electron and ion microprobe analysis, they identified average water

contents of 4.5 wt.% and 3.5 wt.%, respectively, with broader ranges spanning 0.5–8.0 wt.%. These independent data points are remarkably consistent with the values derived from our clinopyroxene analysis and reinforce the interpretation that dacite-hosted clinopyroxenes re-equilibrated with a highly hydrous dacitic melt.

Geodynamic significance

While the calculated values may not perfectly represent the pristine “primary” melt due to re-equilibration (in dacites) or minor diffusional hydrogen loss (in MMEs), they consistently indicate high water concentrations. This hydrous signature is entirely consistent with the regional geodynamic context of the Gutâi Mountains – a post-collisional volcanic setting where the mantle source region was significantly modified by subduction-derived components (Kovács et al. 2017).

Conclusions

Based on our results, it can be concluded that Nominally Anhydrous Minerals (NAMs) in complex calc-alkaline systems, such as the Laleaua Albă composite dacite dike, serve as effective tracers for magmatic evolution. By utilizing clinopyroxene – an early-crystallizing phase originating from a common source for both the dacite and the MMEs – magma-mixing processes can be identified. Specifically, clinopyroxene re-equilibration within melts of varying water contents results in distinct spectral and concentration signatures compared to original magmatic values (Fig. 9).

Furthermore, the NAMs collectively provide critical information regarding the post-emplacement cooling history of the dike. Clinopyroxenes within the studied MMEs, likely situated at the core of the dike, probably experienced slower cooling rates than those in the dacite closer to the country rock, resulting in lower structurally bound hydroxyl (OH⁻) values (Fig. 12). However, the Laleaua Albă composite dike did not undergo complete degassing during cooling; had it done so, the NAMs would have lost their structurally bound hydroxyl content due to prolonged exposure to low water-activity environments.

Our study provides additional evidence that NAMs from subvolcanic bodies can preserve their original structurally bound hydroxyl contents under appropriate conditions. Although the clinopyroxenes in the magmatic system beneath Laleaua Albă are early-crystallizing phases from a deep-seated reservoir, the subsequent evolution of the system – including magma mixing and minor diffusional hydroxyl bound hydrogen loss – makes them ideal benchmarks for interpreting the volatile budget of the parental melts in equilibrium with them.

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