New FTIR data from the Oas-Gutai Mts. and post-eruption effects on the water content of phenocrysts

EGU General Assembly

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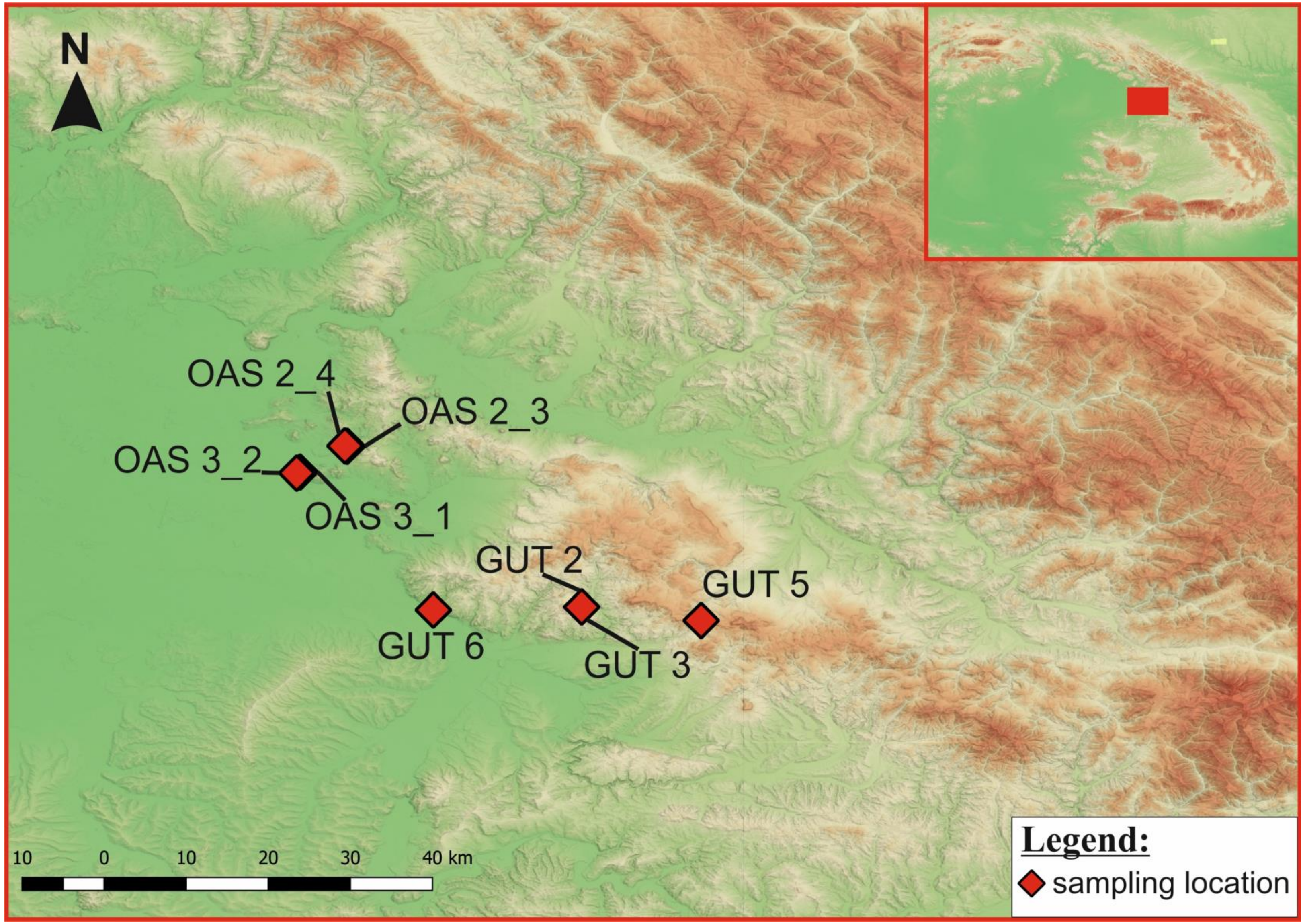
The goal of this study

- The goal of this study is to find rock samples in the study area which contain information about their magmatic water content
- For this purpose we were studying calc-alkaline volcanic rocks of various types from the Oas-Gutai Mts. in Romania
- We used petrography, EMPA and bulk rock geochemistry for the petrogenetic investigation
- For studying the magmatic water content we used **Fo**urier **T**ransform **I**nfrared **S**pectrometry (FTIR) on the **N**ominally **A**nhydrous **M**inerals (NAM's) in the selected samples because based on the FTIR spectra of NAM's we can distinguish the samples that experienced no hydroxyl loss (Patkó et al. 2019)

Geological background

- The Oas-Gutai Mts. is an important part of the Carpathian volcanic range
- Situated on the North-Eastern tip of the ALCAPA microplate separated from the Tisza–Dacia plate by the Dragoş–Vodă fault system (Tischler et al., 2007)
- The subduction related (Kovacs et al., 2017) calc-alkaline volcanism took place between 15.4-7 Ma (Pécskay et al. 2006)



The map of the Oas-Gutai Mts. Showing the sampling locations

Samples

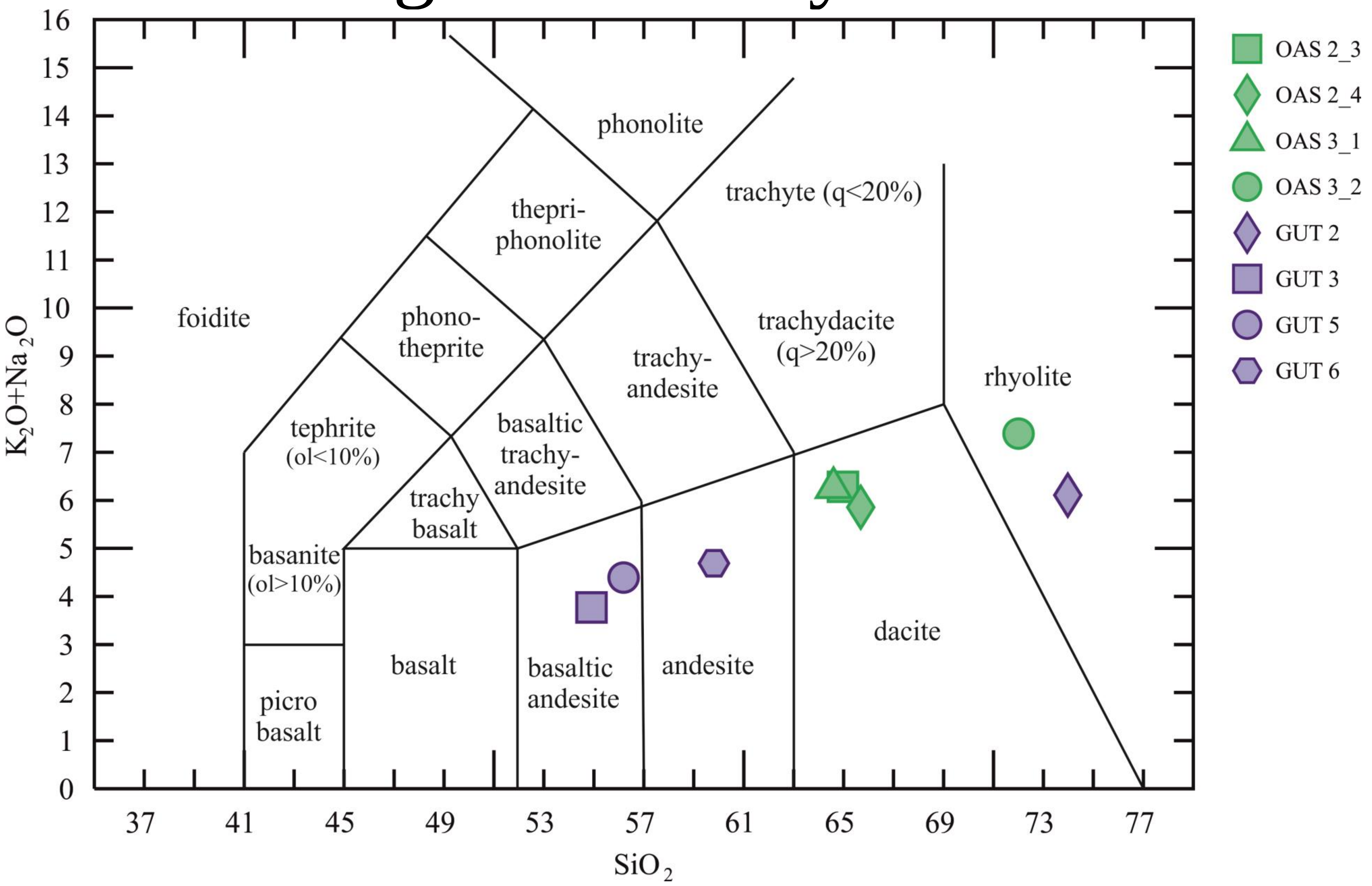
- We studied samples from eight locations, four from Oas and four from Gutai Mts.
- Based on the field observations (shown in the table) the samples are from various rock types with different genetics
- The variety of samples in our study is desirable because according to recent studies (Lloyd et al. 2016, Biró et al., 2017, Pálos et al., 2019) we know that the structural hydroxyl content of NAM's could be modified during and after volcanic eruptions in certain rock types
- Therefore examining different type of rocks than in the previous studies we hope to find samples with unmodified hydroxyl content

Sample code	Rock type	Genetics	Texture
OAS 2_3	dacite	lava	glassy
OAS 2_4	dacite	lava	porphyric
OAS 3_1	dacite	lava	glassy
OAS 3_2	dacite	lava	porphyric
GUT 2	rhyolite	ignimbrite	
GUT 3	basalt	lava	aphanitic
GUT 5	andesite	lava	
GUT 6	andesite	debris avalanche	

The basic field observations of the studied outcrops

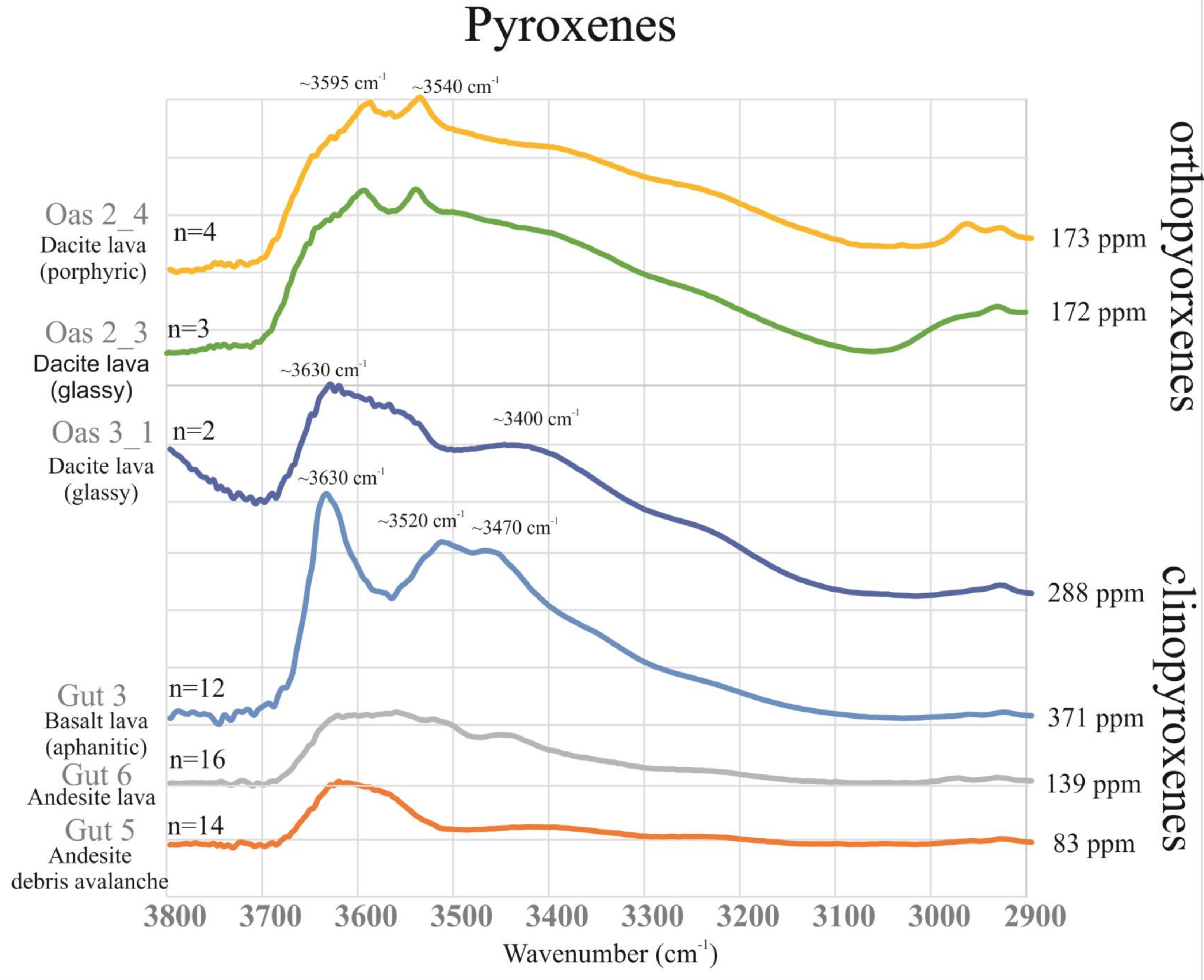
Bulk rock geochemistry

- The studied samples are ranging from basaltic andesites to rhyolites on the TAS diagram (Le Bas et al. 1986) are classified as medium- to high-K rocks according to the Peccerillo–Taylor diagram(Peccerillo and Taylor, 1976)



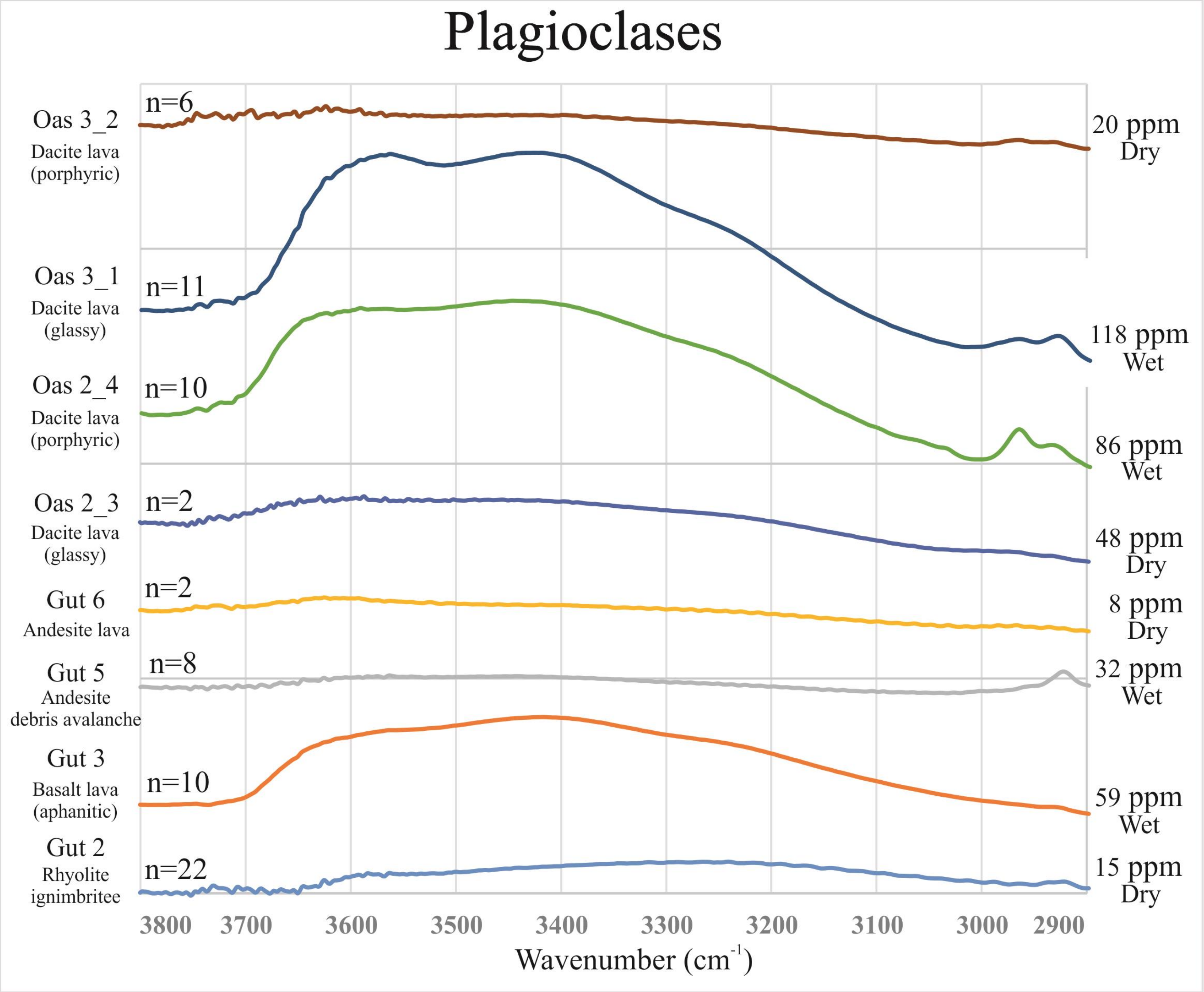
TAS diagram of the analysed samples (Le Bas et al., 1986)

- The observed bands are presented above and hydroxyl content on the right side of the spectra
- The band assignments for clinopyroxenes based on the literature:
  - ~ 3630 cm^{-1} OH^- in T[Si] vacancy (Stalder and Ludwig, 2007; Bromiley et al., 2004)
  - ~ 3520 cm^{-1} $Al^{3+}+H^+ \leftrightarrow Si^{4+}$ (Koch-Müller et al., 2004)
  - ~ 3470 cm^{-1} OH^- in octahedral (M2) vacancy (Smyth et al., 1991)
- The band assignments for orthopyroxenes based on the literature (Stalder and Skogby, 2002):
  - ~3570 cm^{-1} OH^- in T [Si] vacancy or coupled $Al^{3+}+H^+ \leftrightarrow$ T[Si] vacancy
  - ~ 3510 cm^{-1} OH^- in T [Si] vacancy or coupled $Al^{3+}+H^+ \leftrightarrow$ T[Si] vacancy
  - ~ 3395 cm^{-1} OH^- in octahedral vacancy or coupled $Al^{3+}+H^+ \leftrightarrow$ M (octahedral site)



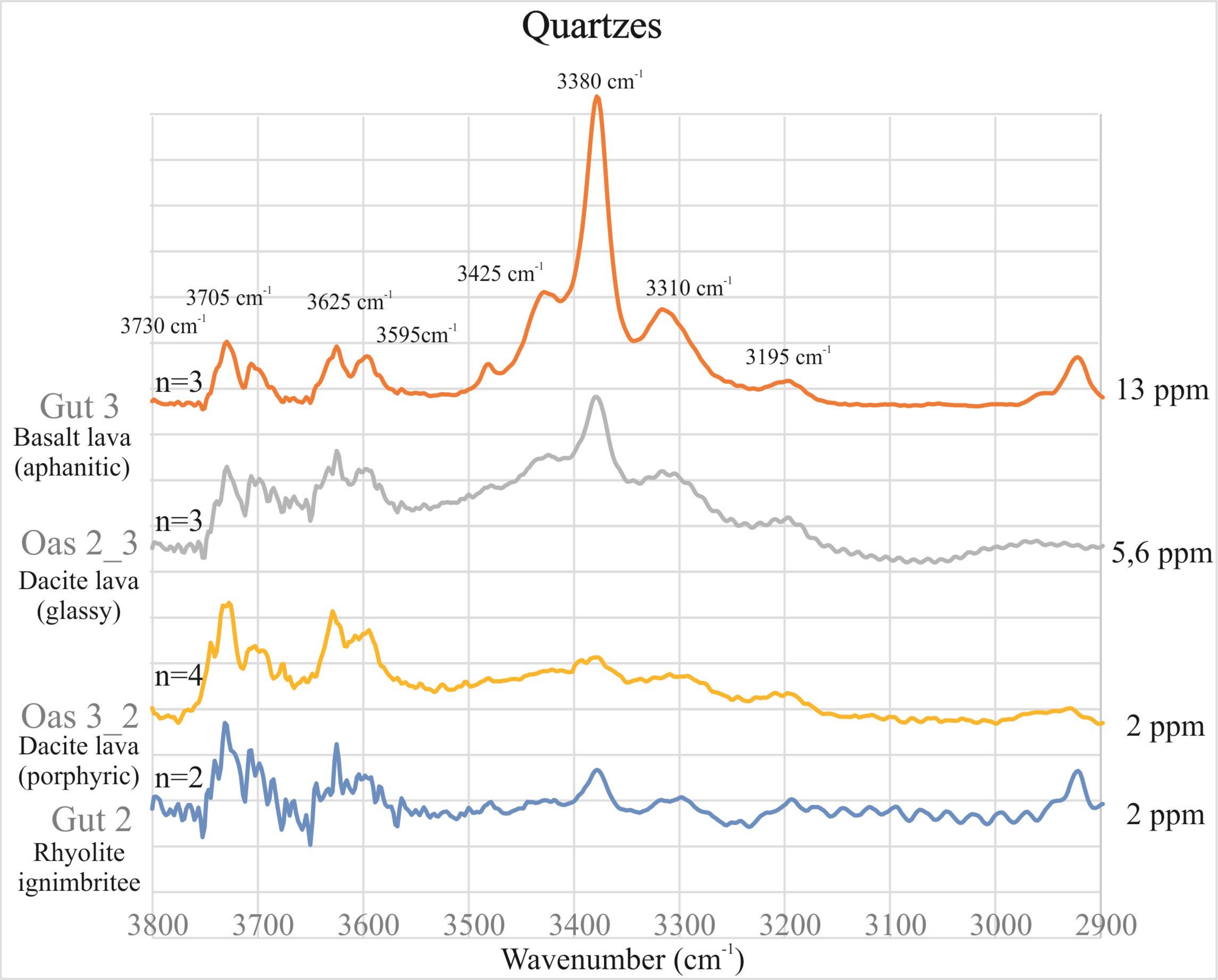
The spectras of the pyroxenes (normalised to1 cm; n-number of spectras evaluated)

- The observed bands are presented above and hydroxyl content on the right side of the spectra
- In case of plagioclase we separated two type of evaluation (noted on the rigth) these are „dry” and „wet”
- In case of „dry” we left out every spectra where the amount of molecular water (based on the size of the band around 3400 cm^{-1}; Johnson and Rossman, 2004) were relatively great
- We only used the „wet” evaluation when the number of meassurments was too low
- It is important to note that in case of the wet evaluation we overestimating the real structural hydroxyl content of the mineral



The spectras of the plagioclasees (normalised to1 cm; n-number of spectras evaluated)

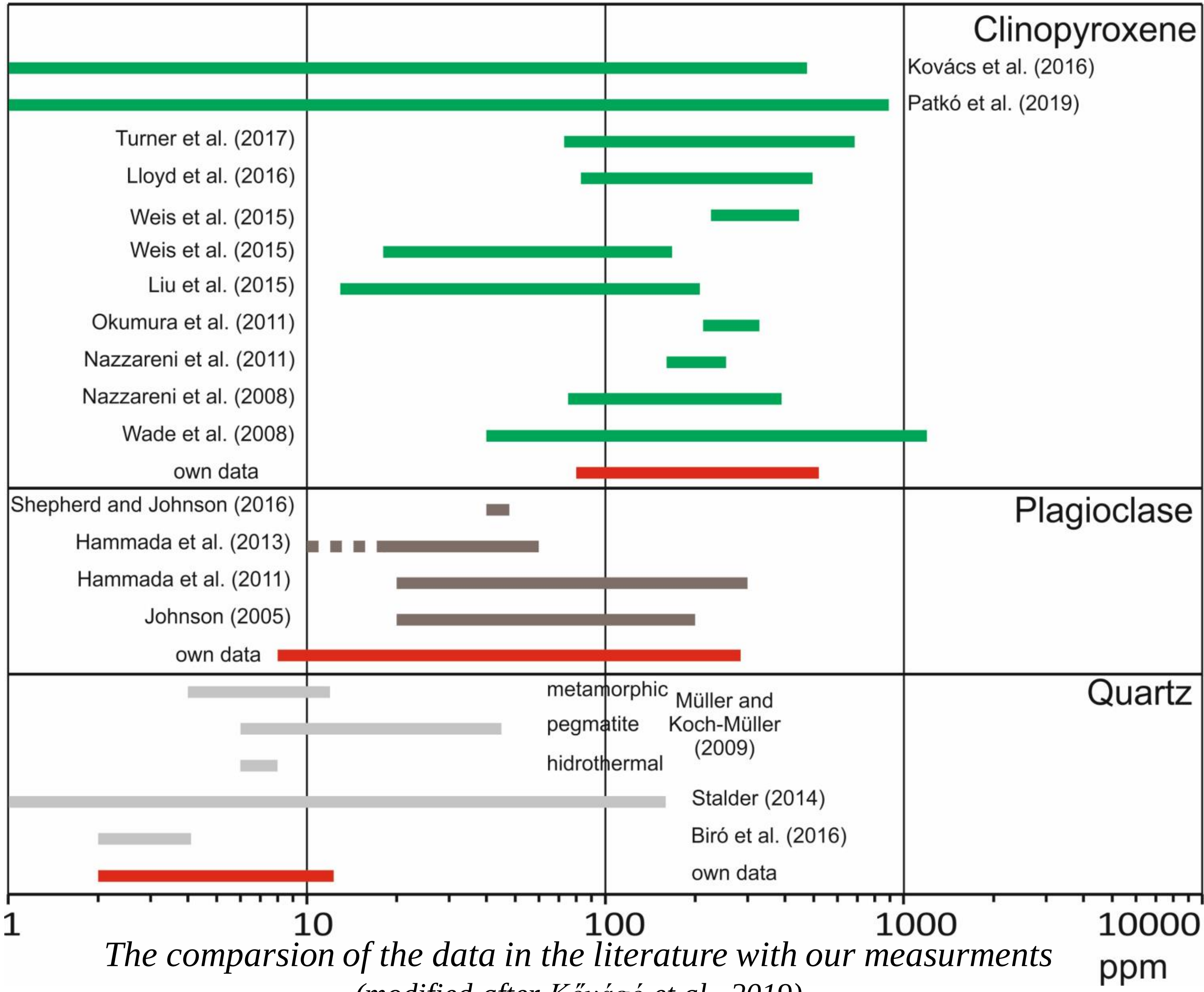
- The observed bands are presented above and hydroxyl content on the right side of the spectra
- The bands around ~3380 cm^{-1}, ~3430 cm^{-1}, ~3315 cm^{-1} are related to the substitution of $Al^{3+}+H^{+} \leftrightarrow Si^{4+}$ (Kats, 1962; Müller & Koch-Müller, 2009; Thomas et al., 2009)



The spectras of the quartzes (normalised to1 cm; n-number of spectras evaluated)

Comprasion of structural hydroxyl contents with the litarature

- The hydroxyl content of the measured NAM's (red) compared to the literature
- The clinopyroxenes shows moderate to high structural hydroxyl contents
- The plagioclases are covering roghly all the values however all of the higher values are from the „wet" evaluation method and representing higher values than the actual hydroxyl content
- The quartz crystals show low to moderate values compared to the whole of the literature



The comparsion of the data in the literature with our measurments (modified after Kővágó et al., 2019)

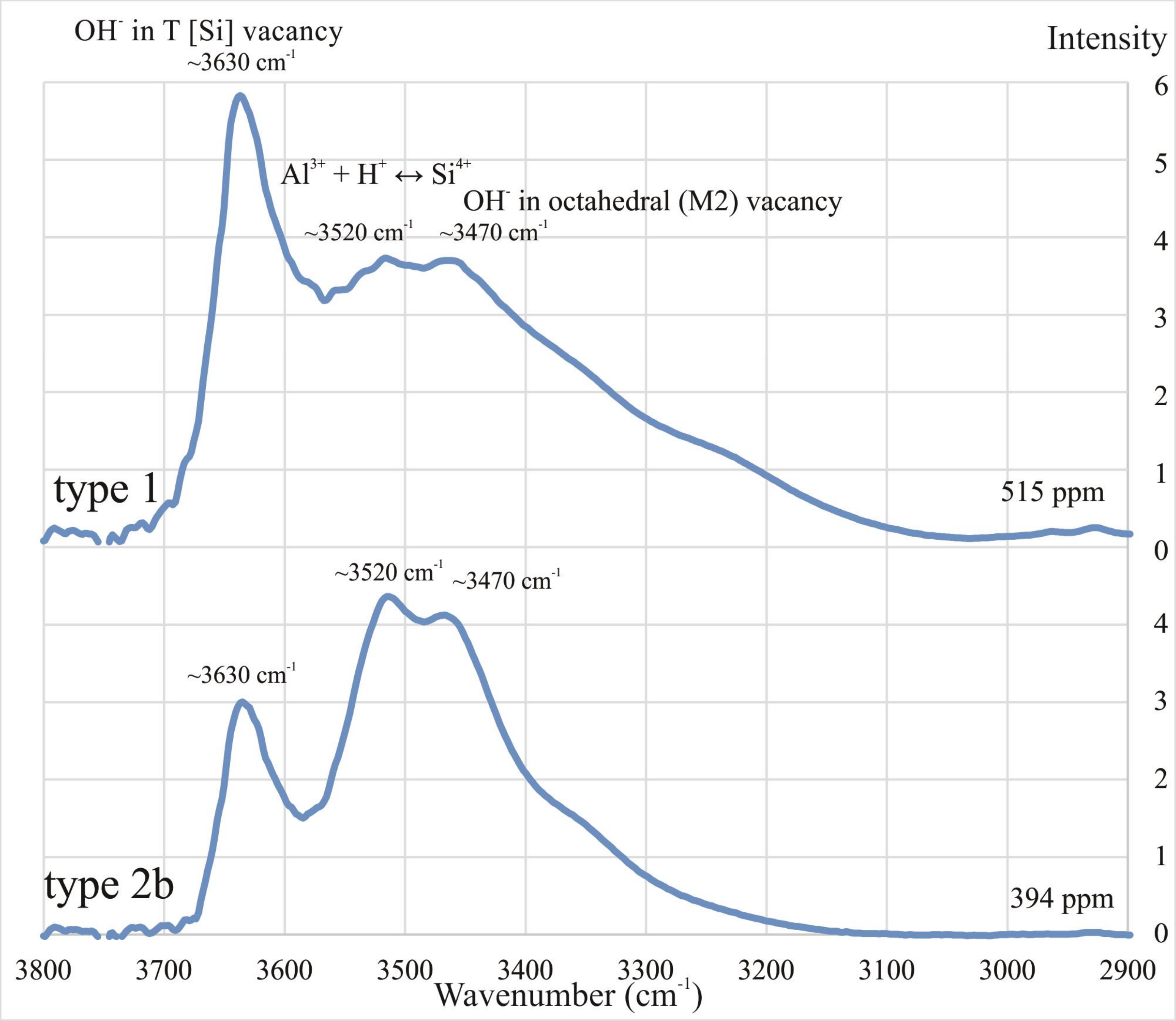
Hydroxyl content of the samples

- Aside from GUT 3 all of the studied samples experienced hydroxyl loss
- If we look at the genetics of the rocks we can see a lot of lava rocks which implies a rather slow cooling after the eruption although GUT 3 is also a lava it was quenched very fast (aphanitic texture) because it consist of small intrusive magmatic bodies
- As for the other types which have a higher possibility to cool fast such as the GUT 2 ignimbrite and GUT 6 debris avalanche unfortunately there was also hydroxyl loss
- Based on the situation of the sample inside the ignimbrite there is a possibility of either losing or retaining the hydroxyl content in NAM’s (Biró et al., 2017)
- As for debris avalanche, it is possible that the analysed sample is from an earlier phase and therefore lost its hydroxyl content due to its more complex origin
- Based on the investigation of the NAM’s the GUT 3 sample is the most promising for studying unmodified structural hydroxyl content because:
  - All of the measured NAM’s contain high concentration of hydroxyl relative to the other samples and the literature
  - The spectra of the clinopyroxene resembles the type 1 spectra reported by Patkó et al. (2019) which is likely representing the original hydroxyl content

Properties of the GUT 3 sample

- The GUT 3 (Firiza basalt) is 7 Ma old, the final product of the magmatism in the Oas-Gutai Mts., composed of small intrusive bodies (Kovacs et al., 2017)
- Based on the petrographic observations the plagiocalses and clinopyroxenes are resorbed and frequently found as glomeroporhyres
- The quartz is present as a xenocryst and surrounded with a clinopyroxene corona which can be a sign of magma mixing or assimilation process (Jurje et al., 2013)
- Chemically both the clinopyroxens and plagioclases shows a relatively primitive composition the clinopyroxenes with an average #Mg of 0,83 (0,63-0,89) and the plagioclases with an average anorthite content of 86,5% (77-92%)
- The clinopyroxenes can classified into two groups based on their Al_2O_3 content, one around 2,7 wt.% and the other around 5,3 wt.%

- More detailed study of the clinopyroxenes revealed that the spectras can divided into two groups based on the work of Patkó et al. (2019)
- The distribution of groups is based on the relative intensities of the absorption bands
- The two groups are the type 1 and type 2b (Patkó et al., 2019)
- The type 1 group is similar to the commonly observed clinopyroxene spectras and likely without hydroxyl loss
- The intensity of the band around 3520 cm^{-1} is related to the Al_2O_3 content, by which the clinopyroxenes can divided into two groups
- Based on this the type 1 has the lower and the type 2b has the higher Al_2O_3 content



The two types of clinopyroxene spectras (normalised to1 cm)

Water content OF GUT 3

- We calculated the equilibrium water content of the Firiza basalts (GUT 3) from the structural hydroxyl content of the clinopyroxenes
- For the partition coefficient calculations we used the method of O’Leary et al. (2010), cation numbers was calculated following the routine outlined in Table A5 of O'Leary et al. (2010)
- For the clinopyroxene compositions we used average values of the two groups (based on Al_2O_3 content)
- The results for the type 1 is 5,2 wt.%H_2O and for the type 2b is 3,1 wt.%H_2O
- We compared this to the results of Kovács et al. (2020): 2.0-2.5 wt.% H_2O; measured on clinopyroxene phenocrysts from alkaline basalts in the BBHVF in the Pannonian Basin
- We also compared these water contents to typical values from basaltic melts in the literature (Dixon et al., 2004; Xia et al., 2013): MORB <0.5; OIB 0.5-1.0; BABB 0.5-2.0; IAB 2.0-8.0 wt%H_2O
- Our values exceeds those of Kovács et al. (2020), MORB, OIB and BABB and falls into the middle of the IAB field

Summary

- Based on the FTIR studies only the GUT 3 retained its original hydroxyl content however the other samples lost most or all of theirs
- The retainment of hydroxyl content in the GUT 3 most likely the result of the fast cooling of the small magmatic bodies due to the contact with the country rock
- According to the intensity of the absorption bands and the chemical data of the clinopyroxenes we can assume that the type 1 has lower Al_2O_3 content than the type 2b
- The calculated equilibrium water content (3,1-5,2 wt.%) compared to the literature falls into the field of island arc basalts (2,0-8,0 wt.%)
- The samples from GUT 3 is good material for future studies of structural hydroxyl and magmatic water content

Thank you for your kind attention!

Supported by NKFIH-K128112
of the Hungarian government

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