





Short Paper

Assessing trace-element mobility during alteration of rhyolite tephra from the Dinaride Lake System using glass-phase and clay-separate laser ablation inductively coupled plasma mass spectrometry

Luka Badurina*  and Branimir Šegvić 

Texas Tech University, Department of Geosciences, Lubbock, TX 79409, USA

Abstract

This paper reports a novel approach in the study of trace-element mobility during the argillization of volcanic glass that is based on *in situ* laser ablation inductively coupled plasma mass spectrometry glass analyses and that of spatially related illite-smectite collected in the form of fraction separates. The material studied originates from lacustrine sediments of the Dinaride Lake System that bear evidence of intensive weathering of distal tephra during the Miocene climatic optimum. Yttrium and HREE were probably mobilized from decomposing glass in the form of carbonate complexes and were consequently depleted significantly in the clays studied. On the other hand, the Mg-rich illite-smectite demonstrates an elevated adsorption potential of solvated LREE complexes. This may be explained through clay surface geochemistry controlled largely by Mg for Al octahedral substitution. This paper highlights the role of eogenetic 2:1 clay aluminosilicates that, under favourable geological conditions, may be conducive to secondary REE enrichment and the formation of potential ion adsorption-type deposits.

Keywords: bentonite, Dinarides, glass alteration, illite-smectite, LA-ICP-MS, REE, trace elements

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Altered volcanic ash may provide insights into the dynamics of trace-element depletion and enrichment during the low-temperature, post-emplacement alteration of primary igneous lithologies due to the increased solubility of trace elements under such conditions (McHenry, 2009; Hong *et al.*, 2019; Namayandeh *et al.*, 2020). Distal volcanic tephra, and ash in particular, consist largely of metastable volcanic glass, which is prone to deuteric alteration in aqueous environments (Christidis & Huff, 2009; Huff, 2016). A comparison between fresh tephra and its alteration derivatives therefore offers an excellent medium to investigate trace-element post-emplacement trajectories (Summa & Verosub, 1992; McHenry, 2009). Several studies have utilized this approach to demonstrate element behaviour during glass argillization and zeolitization in marine and freshwater environments (Christidis, 1998; McHenry, 2009; Kiipli *et al.*, 2017; Hong *et al.*, 2019). These studies were focused on residual elements to infer material provenance and the variations in trace element contents were used to reconstruct the physico-chemical character of the depositional environment. The aforementioned research relied on sampling from various localities (i.e. fresh vs altered) followed by whole-rock geochemical analyses of the collected samples. This approach required relatively large

amounts of analysed material and was prone to possible contamination by non-authigenic detritus. The present study attempts to reconstruct trace-element mobility patterns by investigating the spatially associated fresh volcanic material and the clay minerals it produces. Two samples of partially altered Miocene volcanic ash from the Dinaride Lake System (DLS; Fig. 1; Krstić *et al.*, 2001; de Leeuw *et al.*, 2011; Mandić *et al.*, 2011; Šegvić *et al.*, 2014; Badurina *et al.*, 2021) were selected for laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) *in situ* analyses of glass shards and their respective clay (<2 µm) separates.

This enabled direct assessment of trace-element content in spatially related parent/daughter materials based on very-low-volume analyses of glass shards and tiny amounts of clay separate (~50 mg). X-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) observations were used to characterize the mineralogy and geochemistry of the clay minerals and to identify the possible presence of detrital components.

Materials and methods

Material for this study was recovered from the central DLS localities of Glavice and Tušnica (Croatia and Bosnia and Herzegovina, respectively; Fig. 1; de Leeuw *et al.*, 2011; Šegvić *et al.*, 2014; Badurina *et al.*, 2021). Bulk and clay-fraction XRD analyses were carried out at the Geosciences Clay Laboratory of

*Email: luka.badurina@ttu.edu

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Fig. 1. Geographical map of the sampling localities (modified after Badurina *et al.*, 2021).

Texas Tech University (TTU; analytical details by Šegvić *et al.*, 2020). Measurements were performed using a step scan in the Bragg–Brentano geometry with Cu- $K\alpha$ radiation (40 kV and 40 mA) and a counting time of 3.5 s per $0.019^\circ 2\theta$ from 3.8 to $70^\circ 2\theta$ for bulk fractions, which was modified to 2.3 s per step count from 3.8 to $33^\circ 2\theta$ for clay-fraction measurements. The infrared-attenuated total reflectance (IR-ATR) spectra at ambient conditions were collected using a Perkin Elmer Frontier MIR spectrometer, installed in the same laboratory, in a range of 800 – 1100 cm^{-1} with a spectral resolution of 2 cm^{-1} . The SEM-EDS analyses were performed at the Microscopy Center of the College of Arts and Sciences of TTU as described by Badurina *et al.* (2021). Tuff sections containing glass shards were prepared in the form of thick (~ 100 μm) sections and analysed using LA-ICP-MS at the TTU GeoAnalytical Laboratory (analytical details in Šegvić *et al.*, 2021). Si abundances determined using EDS were utilized as internal reduction standards. The clay fractions from the studied samples were separated using centrifugation (Šegvić *et al.*, 2021) and then investigated using a LA-ICP-MS line raster analysis (Table S1), which has been proven to be suitable for the study of an inherently heterogeneous clay material (Vannoorenberghe *et al.*, 2020). The time-resolved LA-ICP-MS signal was inspected for possible contamination. The matrix-appropriate standards Jsd-1 and USGS BHVO-2 G (Jochum *et al.*, 2005; Nath *et al.*, 2009) served as measures of the method's precision and accuracy (Table S1).

Results and discussion

Mixed-layer illite-smectite (Ilt-Sme) accompanied by minor amounts of illite, kaolinite, tridymite, quartz, feldspar and gypsum make up the bulk mineralogy of the analysed tephra (Fig. 2a,b). The prominent 15 – $35^\circ 2\theta$ hump in the XRD traces (Fig. 2a,b) is attributed to the presence of volcanic glass and possibly amorphous silica (i.e. opal-A). The XRD traces of the bulk samples and the clay fractions of both samples show a predominance of highly crystalline Ilt-Sme. This is somewhat less pronounced in the case of the

Glavice sample, which encompasses multiple Ilt-Sme generations of lower crystallinity. The relative positions of the Ilt-Sme 002/003 peaks (15.78 vs $15.69^\circ 2\theta$) combined with the 001/002 and 002/003 $\Delta^\circ 2\theta$ values (5.33 vs $5.31^\circ 2\theta$; Moore & Reynolds, 1997) suggest a Sme-rich (i.e. $>90\%$) Ilt-Sme in both clay fractions, with the Glavice sample probably having a slightly greater Sme content.

The IR-ATR spectra in both samples reveal Si–O and Al–Al–OH bands at ~ 990 and 914 cm^{-1} , respectively (Fig. 2c,d). The Tušnica sample features an 843 cm^{-1} Al–Mg–OH band, while the Glavice sample displays an Al–Fe–OH band at 875 cm^{-1} (Fig. 2c,d; Madejová *et al.*, 2017).

The SEM-EDS analyses reveal glass shards of essentially constant chemical composition that seem to be coated with Ilt-Sme of variable morphology (Table 1). Ilt-Sme outgrowths of similar phase chemistry emerge readily from the glassy substrate (Fig. 2e).

In the case of the Tušnica clays, the Ilt-Sme crystals are up to ~ 0.3 – 2.0 μm long (Fig. 2e & Table 1). Conversely, the size of Ilt-Sme in the Glavice clays is smaller, being within the sub-micron range. These clays form aggregates with a typical honeycomb texture (Christidis, 2010) found as glass vesicle infills (Fig. 2f). In comparison with volcanic glass, the observed clay minerals are depleted in SiO_2 and alkalis while being enriched in all other oxides. The FeO and TiO_2 in the clay minerals may be related to the decomposition of igneous phases such as biotite, while the increased MgO and CaO are attributed to the availability of these cations in karstic lake waters (Sironić *et al.*, 2017). With reference to the Tušnica clays, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of Ilt-Sme in the Glavice clays is greater (3.8 vs 3.5 ; Table 1), which is consistent with the XRD data. The K and Na contents of the Glavice clays are greater than those of the Tušnica clays (1.8 vs 0.8 wt.% and 1.0 vs 0.6 wt.%, respectively; Table 1), while the octahedral Mg content seems to be halved (Fig. 2c & Table 1).

Chondrite-normalized LA-ICP-MS analyses of the volcanic glass revealed an evolved igneous character (LREE enrichment

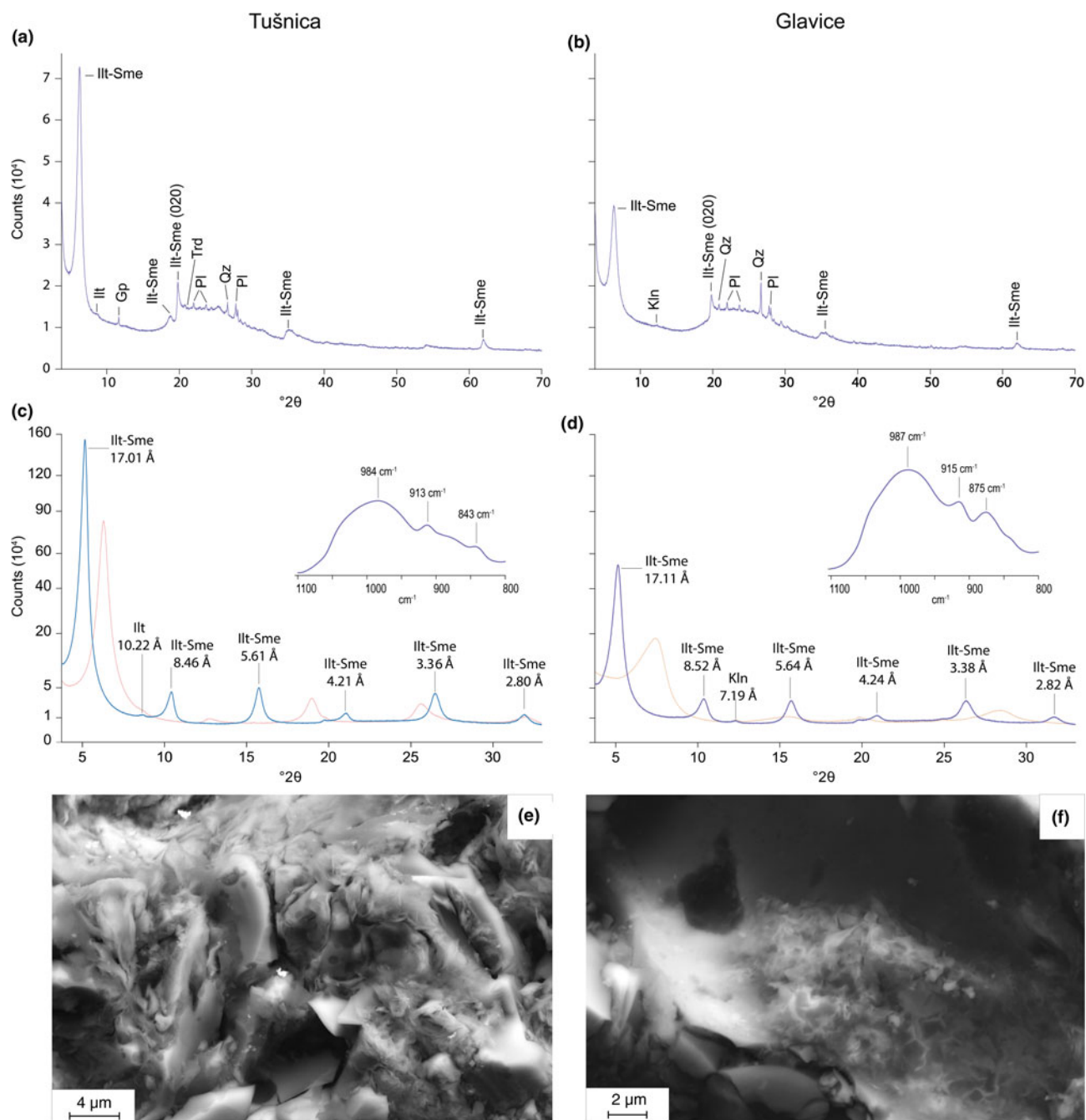


Fig. 2. XRD traces of (a,b) bulk and (c,d) clay fractions (<2 μm). The insets indicate FTIR spectra of the clay fractions. The red and blue lines in the XRD traces of the clay fractions correspond to air-dried and ethylene glycol-solvated samples, respectively. The y-axis values were square-root transformed to assist with the correlation. (e,f) SEM images of the Tušnica and Glavice samples, respectively. Illt-Sme = illite-smectite; Illt = illite; Kln = kaolinite; Trd = tridymite; Qz = quartz; Gp = gypsum; Pl = plagioclase.

(La_N/Yb_N (Tušnica) = 3.5, La_N/Yb_N (Glavice) = 8.6), Eu anomaly (Eu^* (Tušnica) = 0.3, Eu^* (Glavice) = 0.4; Fig. 3a,b & Table 1).

The same normalization applied to the REE of the clay fractions resulted in greater LREE/HREE ratios (La_N/Yb_N (Tušnica) = 12.8, La_N/Yb_N (Glavice) = 20.5; Fig. 3a,b & Table 1) and Eu anomalies of reduced intensities (Eu^* (Tušnica) = 0.4, Eu^* (Glavice) = 0.5). To inspect trace-element mobility during the argillization of volcanic glass, we first normalized the clay and glass Y and REE contents to the respective Al_2O_3 concentrations

of the samples. The two normalized samples were then compared against each other using the equation of Nesbitt (1979) (Fig. 3c,d). Both samples feature similar rates of Y and HREE depletion (~70%) and positive Eu anomalies (Fig. 3c,d). The LREE depletion rate of the Glavice clays remains flat at ~40%, while in the Tušnica clays the LREE tends to deplete systematically (~7 to ~40% loss; Fig. 3d).

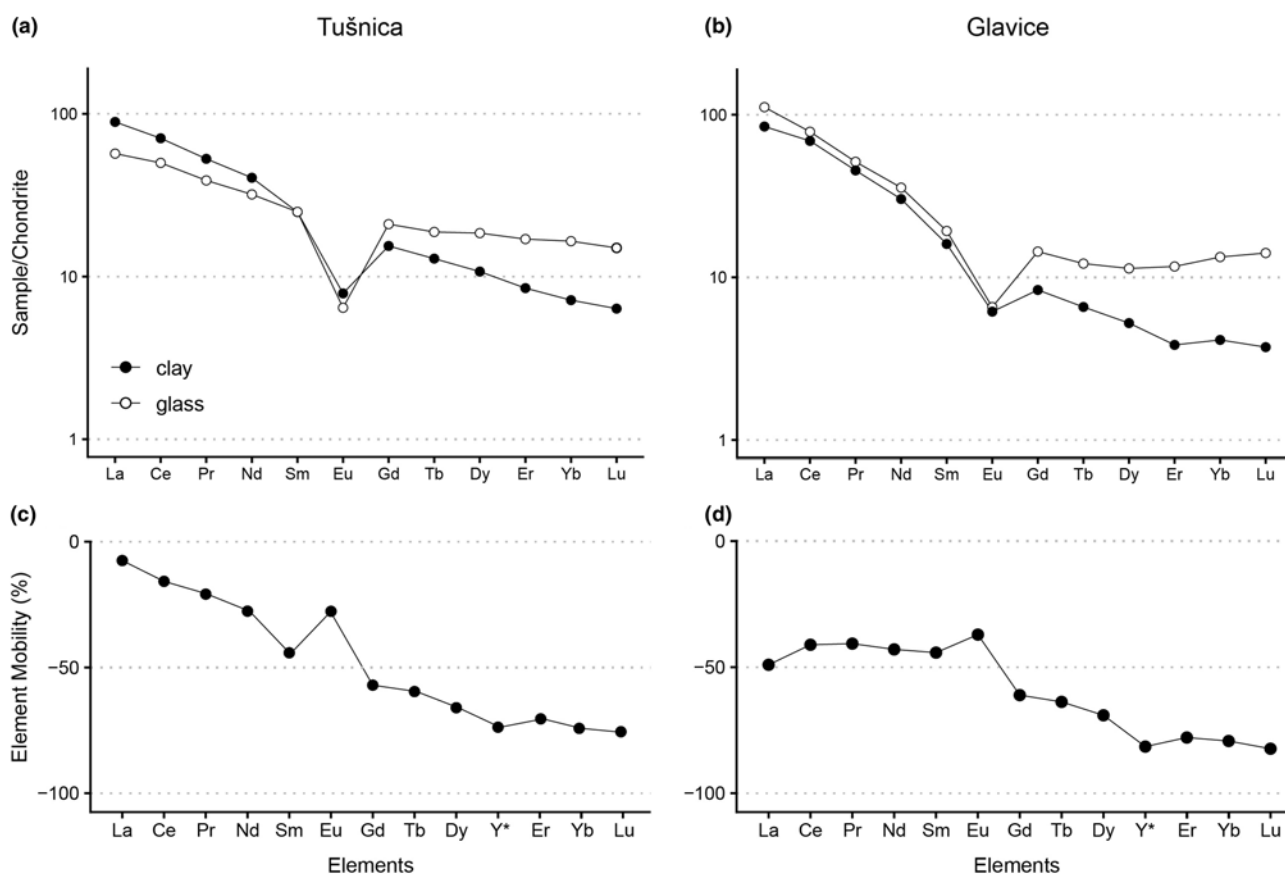
The high rates of Y and HREE depletion in the Illt-Sme studied herein may be attributed to carbonate complexation of those

Table 1. EDS and LA-ICP-MS analyses of the studied tuff. Major oxides and trace elements are expressed in wt.% and ppm, respectively.

Sample	SiO ₂	Al ₂ O ₃	FeO	MgO	CaO	K ₂ O	Na ₂ O	TiO ₂	SiO ₂ /Al ₂ O ₃	Y
Tušnica glass	79.9	12.4	bdl	bdl	1.9	3.9	1.9	bdl	6.5	38.01
Glavice glass	78.3	12.3	1.5	bdl	1.3	4.8	2.7	bdl	6.4	25.56
Tušnica clay	71.9	20.7	0.9	4.1	2.1	0.8	0.6	1.0	3.5	16.78
Glavice clay	69.3	18.4	2.8	1.7	4.2	1.8	1.0	bdl	3.8	7.05

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Er	Yb	Lu
Tušnica glass	17.79	40.40	4.85	19.97	5.18	0.48	5.53	0.90	6.04	3.59	3.45	0.50
Glavice glass	34.51	63.50	6.27	21.36	3.76	0.48	3.73	0.58	3.65	2.45	2.79	0.45
Tušnica clay	27.68	57.22	6.46	24.30	4.86	0.58	3.99	0.61	3.45	1.78	1.50	0.20
Glavice clay	26.23	55.77	5.55	18.18	3.13	0.45	2.16	0.31	1.68	0.81	0.86	0.12

bdl = below detection limit.

**Fig. 3.** (a,b) Chondrite-normalized plots (Boynnton, 1984) and (c,d) element mobility plots of the analysed samples.

elements and limited adsorption of these complexes on the clay mineral surfaces (Byrne & Kim, 1990; Sholkovitz *et al.*, 1994). Various carbonate species presumably were abundant in karstic lakes such as the DLS (Cantrell & Byrne, 1987; Möller & Bau, 1993; Christidis, 1998). In such environments, the REE distribution is controlled by sorption (Chen *et al.*, 2015), and a positive Eu anomaly as depicted in the mobility diagrams (Fig. 3c,d) commonly is related to plagioclase weathering (Weill & Drake, 1973; Christidis, 1998). However, the DLS tephra is poor in plagioclase (Šegvić *et al.*, 2014); therefore, the Eu anomaly reflects a preferential mobilization of divalent Eu in anoxic porewaters rich in organic matter (Bau, 1991; Hong *et al.*, 2019). The latter probably

was derived from the neighbouring coal layer in the Tušnica clays (Badurina *et al.*, 2021). Particles of Ill-Sme are dominated by their basal siloxane surfaces, which are the least reactive surfaces in clay minerals (Schoonheydt & Johnston, 2013). However, in the case of isomorphism and particularly octahedral substitution of Al by Mg, the charge deficit is delocalized over the surface oxygen atoms of siloxane planes (Sposito *et al.*, 1999). This represents a favourable adsorption domain for solvated cations such as LREE, which are suggested to vacate the glass in the form eight- or nine-fold hydrated outer-sphere complexes (Borst *et al.*, 2020). A relatively great Mg content in the Tušnica clays, as is corroborated by the FTIR (Fig. 2c) and EDS spectra (Table 1), may

therefore explain the pronounced *LREE* retention potential of these clays.

Conversely, the smaller particle size of the Glavice clays (Fig. 2f), which leads to a greater density of edge/defect charges, probably played a secondary role in *LREE* adsorption. Finally, the octahedral sheet of the Ilt-Sme in the Glavice clays seems to host Fe, which, in addition to the substitution of Mg by Al (Table 1), is further supported by the noticeable FTIR Al–Fe–OH band (inset in Fig. 2d). Under the oxidizing conditions that prevailed in Lake Sinj (Glavice locality; Vranjković, 2011), structural Fe³⁺ did not contribute to permanent structural charge and therefore had no impact on the surface geochemistry of the Ilt-Sme.

Conclusions

This study has demonstrated that meaningful geochemical data can be collected from small volumes of a clay fraction (~50 mg) and individual glass shards to reconstruct the behaviour of trace elements during the argillization of pyroclastites in aqueous media. This enables analysis of spatially related parent and daughter materials, thus enabling the detection of possible (detrital) contamination. This approach is also useful for studying scarce materials from drill holes devoid of fresh equivalents. Subject to future investigation, this study has also shown that, in the case of 2:1 clay minerals (i.e. mixed-layer Ilt-Sme), it is their octahedral substitution that exercises primary control over the clay surface geochemistry. This gives rise to reasonably strong adsorption of the solvated complexes of trace elements. Our preliminary study focuses on the lacustrine environments of the DLS, where sub-tropical Miocene weathering of distal tephra produced clay assemblages with *REE* adsorption potential.

Supplementary material. To view supplementary material for this article, please visit <https://doi.org/10.1180/clm.2022.12>

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