Chapter

Submarine Stratovolcano Peperite Syn-Formational Alteration - A Case Study of the Oligocene Smrekovec Volcanic Complex, Slovenia

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Abstract

The Oligocene Smrekovec Volcanic Complex is a remnant of a submarine composite stratovolcano with a complex succession of lavas, autoclastic, pyroclastic, syn-eruptive resedimented volcaniclastic and siliciclastic deposits was a favourable environment for the development of peperites. Despite very complex alteration related to the stratovolcano-hosted hydrothermal system with a deep igneous source, locally elevated geothermal gradients and superimposed hydrothermal/geothermal regimes controlled by the emplacement of a shallow intrusive body, authigenic minerals in peperites - particularly pumpellyite and actinolite - show higher temperature stability ranges than those in the underlying and overlying volcanic deposits irrespectively of their lithofacies, porosity and permeability. The formation of authigenic minerals in peperites, such as laumontite, pumpellyite, epidote, prehnite or actinolite, was apparently controlled by ephemeral and localised high-temperature regimes originating from the parent lava flow. Heated pore waters in the host sediment that could have undergone local mixing with deuteric fluids circulated in peperites until thermal gradients persisted, and were the cause of alteration of juvenile clasts and the mingling sediment. The development of pumpellyite required a suitable precursor - fine-grained volcanic ash.

Keywords: peperites, autoclasic deposits, hydrothermal alteration, submarine composite stratovolcano, Oligocene volcanism

1. Introduction

Peperite is a volcaniclastic rock related to *in situ* disintegration of magma intruding and mingling with the host sediment that is unconsolidated or poorly consolidated, and typically wet [1]. Peperite commonly occurs along the contacts between intrusions and wet sediments and at the base of lava flows overriding or indenting wet sediments [2–4]. The composition and texture of magmas involved in the formation of peperites may range from basaltic to rhyolitic and aphanitic to porphyritic, respectively, and the mingling sediments may have rather diverse texture, grain size and composition. As the availability of wet unconsolidated sediments is a prerequisite for the development of peperites they have been commonly encountered in submarine environments with contemporaneous volcanic activity and sedimentation, such as volcanic arcs and back-arc basins [5–9].

The formation of peperite is a complex process and depends, in general, on the magma and host sediment properties, their mass ratio and total volume of pore water heated during their contact and mingling. For magma, the most relevant properties are composition, the content of volatiles and rheology, and for the host sediment that is texture and water-saturation. An important stage in the process of peperite formation is magma disintegration that can be brittle or ductile and attained by quenching, hydromagmatic explosions, surface tension effects, mechanical stress related to the movement of magma and density contrast to the sediment, and magma-sediment shearing. The contact of magma and wet sediment causes heating and expansion of pore waters, and the resulting disruption of coherence and sometimes fluidisation and shear liquefaction of the host sediment facilitate dispersion of clasts derived from magma away from the site of formation. The intricate processes of intermixing finally result in the formation of peperite [4, 10–14].

Two textural types of peperite have been recognised on the basis of shape of clasts derived from magma. Blocky peperite consists of sharply angular, blocky or platy clasts while in globular or fluidal peperite lensoidal, lobate, ameboid or bulbous clasts occur [5]. The term peperitic hyaloclastite refers to a peperitic rock in which magma fragmentation is largely the result of quenching, mechanical stress, or pore-water steam explosions [4, 12].

Several detailed studies of peperite occurrence and formation have been carried out in the system of Pannonian basins, in particular, in the Tokaj Mountains [15] and Western Hungary at Hajagos-hegy, Kissomlyó and Ság-hegy [9, 16, 17]. Subaqueous Miocene rhyolitic dome-cryptodome complex outcropping at Pálháza, the Tokaj Mountains, is surrounded by a carapace of hyaloclastites, hyaloclastite breccia, and globular and blocky peperite. Closely packed peperite zone with jigsaw-fit juvenile clasts formed next to a rhyodacitic body, and toward the boundary with the host sediment, a transition into the clast-rotated and clast dispersed zones of peperite has been recognised [17]. In the volcanic conduits, vents and crater lakes of phreatomagmatic volcanoes in Mio/Pliocene volcanic fields of Western Hungary globular and blocky peperite occur together regardless of the grain-size and texture of host sediment [15]. The study supports conclusions that the formation of different peperite textures depends on several factors, e.g., break-down of vapour films at the magma/wet-sediment interface, viscosity of magma and/or magma flux rate, a change in temperature, microlite crystallinity and gas content of magma, thermal properties of the host sediment and steam explosions [18–22].

The alteration of peperite is common and may begin contemporaneously to its formation owing to the release of deuteric magmatic fluids and volatiles, transfer of heat from magma or lava to the host sediment and heating of pore-waters therein. Large magma intrusions can cause contact metamorphism along the margins and initiate or modify fluid circulation on a several-kilometre-scale that may last a long period of time after the peperite formed [23]. Lavas undergo more rapid cooling, and effective circulation of heated pore-waters can be attained only locally along the contacts with the wet sediment until thermal gradients exist. Most often, the formation of secondary minerals such as carbonates, Fe-oxides and silica along the contacts of juvenile clasts has been reported [23–27].

The Oligocene Smrekovec Volcanic Complex (**Figures 1** and **2**) located in the south-westernmost extending of the Tertiary system of Pannonian basins, is a remnant of a submarine stratovolcano. Prior to erosion, and tectonic dissection and displacement along the Periadriatic Line, the stratovolcano extended in an area

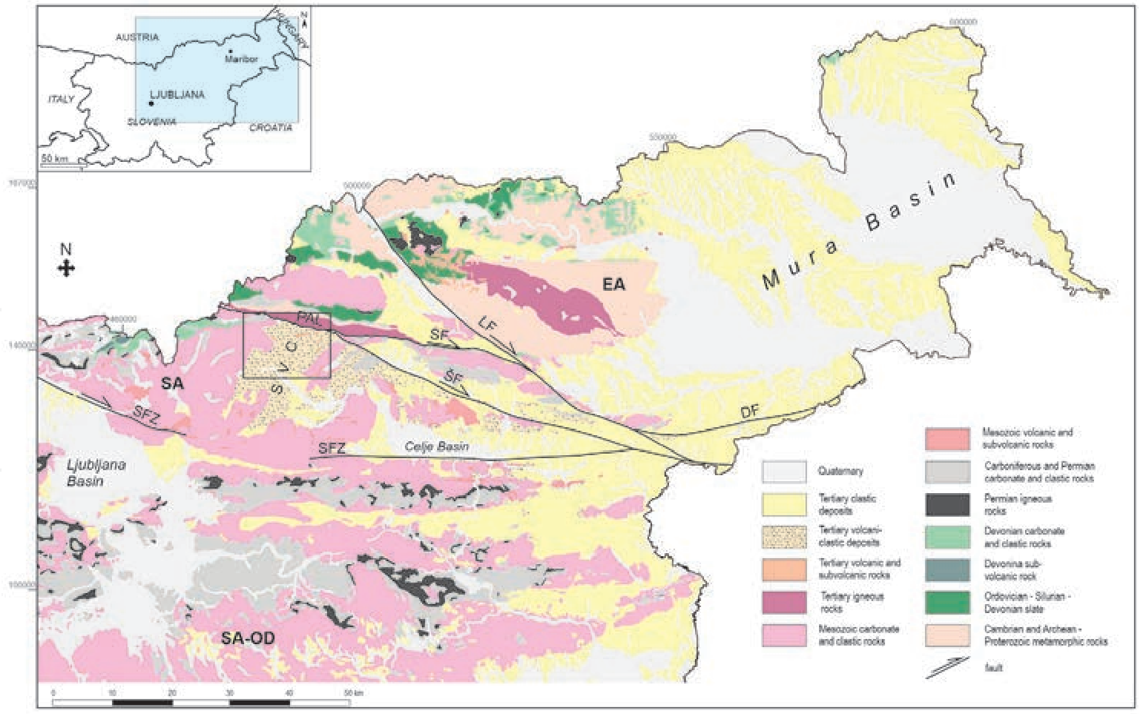

Figure 1.
Simplified geological map of northern Slovenia after [28, 29] with the study area (framed) in the Smrekovec volcanic complex (SVC). PAL -Periadriatic Line; LF – Lavanttal (Labot) fault; SF – Smrekovec fault; ŠF – Šoštanj fault; DF- Donat fault; SFZ – Sava fault zone; SA – Southern Alps; EA – Eastern Alps; OD – Outer Dinarides.

of over 1000 km^2. Similar large submarine volcanoes have been encountered in modern and ancient environments worldwide (e.g., [30–32]), and also, within the Carpathian-Pannonian region [33–35].

The stratovolcano is composed of a succession of lavas and shallow intrusive bodies, and autoclastic, pyroclastic, resedimented volcaniclastic and mixed siliciclastic-volcaniclastic deposits. Lithofacies associations change from proximal, medial and distal zones over a distance of 0-2 km, 2-5 km and 5-20 km, respectively. The proximal zone is dominated by lavas and autoclastic deposits, and in the medial-zone pyroclastic and syn-eruptive resedimented volcaniclastic deposits become abundant. The distal zone is dominated by fine-grained pyroclastic, syn-eruptive resedimented volcaniclastic and siliciclastic deposits.

Peperites are the most abundant in medial-zone lithofacies associations. The mingling lavas range in composition from andesitic to rhyodacitic and the host sediments are mixed siliciclastic-volcaniclastic silts and calcareous muds or volcaniclastic deposits of various texture and grain size, i.e., fine- and coarse-grained tuffs, lapilli tuffs, volcaniclastic breccias [36]. Blocky and fluidal peperite and peperitic hyaloclastite are common in occurrence although their formation has not been related to the texture, grain size or porosity of the host sediment.

The stratovolcano-hosted hydrothermal system with convective-advective flow regime developed, and as a result, alteration minerals formed, the most widespread assemblage being laumontite, chlorite, ordered mixed layer chlorite-smectite, quartz and albite. Despite of complex alteration that affected lithofacies associations, peperites very often contain authigenic minerals with typically higher temperature stability ranges than those in the adjacent underlying or overlying volcaniclastic deposits [37, 38]. Their formation must have occurred contemporaneously to the development of the host rock itself owing to thermal gradients originating from the parent lava or shallow intrusive body and geochemical gradients related local circulation of heated pore waters and deuteric fluids.

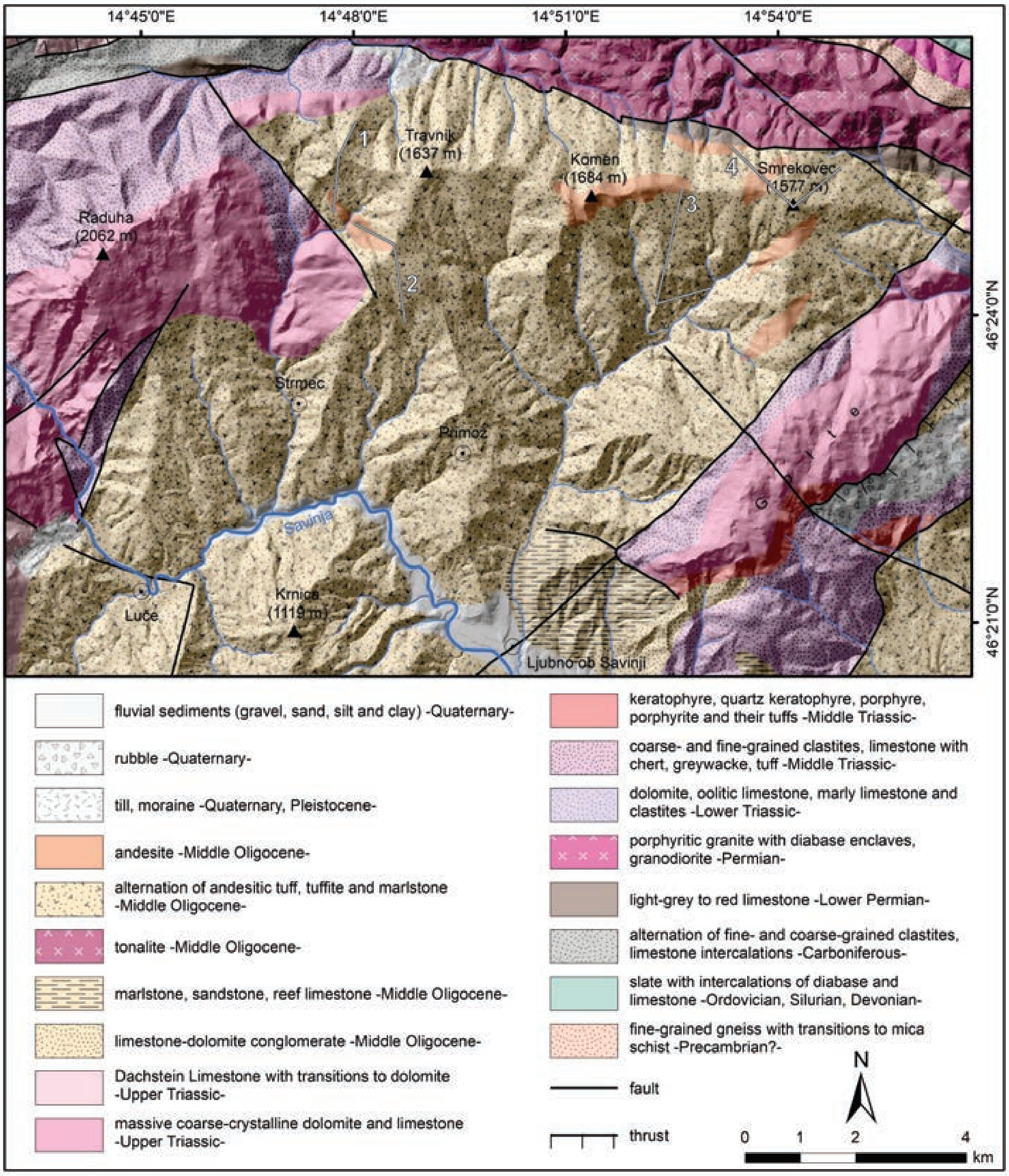

Figure 2.
The study area (northern Smrekovec Volcanic Complex) after [28, 29] and the sections 1 (Presečnik), 2 (Javorec), 3 (Krnes) and 4 (Smrekovec G34). The Kramarica Sill is about 200 m thick and located at the base of the section 4 along the outcrops of lower Permian limestone.

As the Smrekovec Volcanic Complex is a remnant of an ancient submarine composite stratovolcano the processes of alteration of peperites described herein could be recognised in, and applied to, similar environments worldwide.

2. Sampling and analytical techniques

The sampling was performed in the entire area of the Smrekovec Volcanic Complex, although particularly detailed study has been carried out in two sections Krnes, and Smrekovec G34 (**Figure 2**). Lithofacies was determined by field observation, and chemical, mineralogical and petrographic analysis. Over 900 thin sections have been inspected in detail.

Alteration minerals were analysed by X-ray diffraction (XRD) techniques in altogether 260 samples. Zeolites and related calcium aluminosilicate minerals were determined in whole-rock powdered samples. Clay minerals were analysed in oriented samples using slurries (<2 μm) dispersed on glass slides and undergoing standard procedures including air-drying and solvation in ethylene glycol. The XRD analysis was performed using a Philips diffractometer PW 3719 and a goniometer PW 1820, owned by the Department of Geology, Faculty of Natural Sciences and Technology, University of Ljubljana. Machine settings for all analysed samples were as follows: generator operated at 40 kV and 30 mA using CuK_α radiation (wavelengths $K_{\alpha1}$ = 1.54056 Å and $K_{\alpha2}$ = 1.54439 Å), Ni filter, with automatic divergence slit and monochromator on. Scanning rate was 2°2θ/min; scanning range amounted to 2°2θ – 70°2θ for powdered samples and 2°2θ - 45°2θ for oriented samples. Digital data were processed using peak-fitting program X'Pert HighScore Plus 4.0. Semi-quantitative analysis was performed by the program using the data base, internal standard rock samples and bulk chemical composition of powdered samples.

Detailed mineral studies were performed on 9 polished thin sections using a scanning electron microscope (SEM) Jeol JSM-6490 equipped with an energy dispersive spectrometer (EDS) INCA Oxford 250, and located at Geological Survey of Slovenia. Elemental analyses were performed in thin sections having a thickness of 40 μm and uncovered polished upper surface, at accelerating voltage of 15 kV using a defocused electron beam of 20 μm in diameter, with a current of 10 nA and a counting time of 20 s. Synthetic and natural standards were used for calibration.

Chemical analysis of 150 bulk-rock samples of lavas and shallow intrusive bodies was performed in AcmeLabs, Vancouver, Canada, and Actlabs Activation Laboratories Ltd. Ontario, Canada. Major and trace elements were determined by a combination of X-ray fluorescence (XRF), inductively coupled plasma source (ICP) and mass spectroscopy (MS) analytical techniques.

3. Geological setting and the studied sections

In northern Slovenia, there are four large tectonic units: the Eastern Alps, the Southern Alps, the Outer Dinarides and the south-westernmost extending of the Tertiary system of Pannonian basins [28, 29] with the Smrekovec Volcanic Complex (**Figure 1**). The most outstanding geological structure is the Periadriatic Line (PAL), a complex regional fault system which represents in palinspastic reconstructions a shear zone developed by Late Cretaceous to Paleogene subduction of the European plate below the African plate [39, 40]. In the Eocene (~45 Ma) the subduction transformed into collision although the convergence continued during the Oligocene and resulted in break off of the southeast-dipping European slab beneath the Alps that generated magmatism along the PAL [41, 42].

The related Oligocene (28-22 Ma) volcanic activity occurred in the Smrekovec Basin (**Figure 3**) that had been subsided within the Permian and Triassic clastic and carbonate successions [43]. Tertiary sedimentation began in Late Eocene in fluviatile, limnic and shallow-marine depositional environment and changed to outer neritic and bathyal during the Oligocene time [29, 43]. In a middle bathyal environment characterised by sedimentation of organic-rich clayey silts [43], simultaneous volcanic activity created a composite stratovolcano. Magmas had calc-alkaline and medium-K affinity and formed a suite ranging in composition from basaltic andesite to dacite [44–46]. Volcanic activity had entirely submarine character and after its cessation, the Upper Oligocene to Early Miocene (Egerian) sedimentation continued with fossiliferous marine clayey silt [29]. The stratovolcano hosted hydrothermal system with a deep igneous source and convective-advective flow of hydrothermal fluids (**Figure 3**).

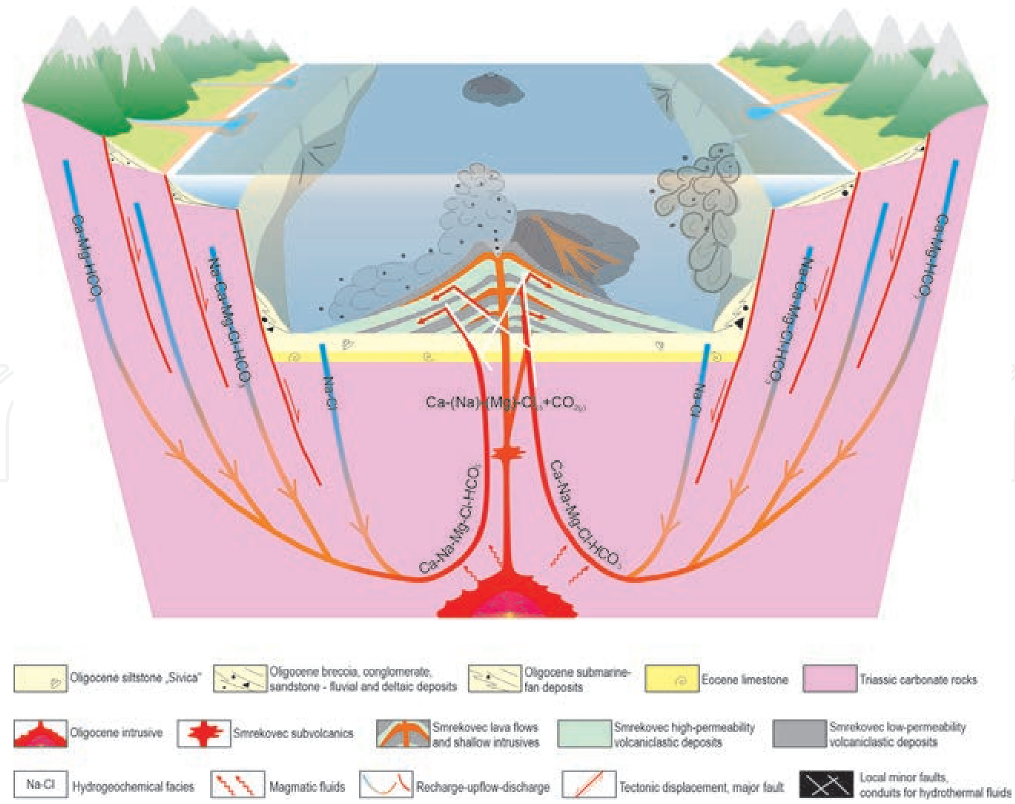

Figure 3.
A conceptual model of the Smrekovec Basin with the stratovolcano and volcanic-hydrothermal system with a deep igneous source of heat and convective-advective flow regime. Hydrothermal fluids originating from heated and chemically modified surface and marine waters ascended through fracture systems and when reached the stratovolcano edifice they outflowed laterally and downward, preferentially through high-permeability layers. High-permeability layers underwent more extensive alteration and the authigenic minerals (e.g., laumontite, prehnite) have higher temperature stability ranges than those in the adjacent underlying or overlying low-permeability layers (e.g., clinoptilolite, heulandite, analcime).

Late Miocene tectonic activity along the Periadriatic Line dissected the stratovolcano edifice and displaced its northern sector in the south-eastern direction on a 100 km scale [29]. The remaining Smrekovec Volcanic Complex probably encompasses about one quarter of the original stratovolcano edifice [36], and scarce outcroppings of volcanic rocks occurring north of the Šoštanj fault (**Figure 1**) are the assumed displaced remnants [47]. South of the Šoštanj fault Tertiary volcanic deposits occur in the Celje Basin, and together with the Smrekovec Volcanic Complex they are united in a lithostratigraphic unit termed the Smrekovec Series [29].

The succession of lavas, shallow intrusive bodies, and autoclastic, pyroclastic, syn-eruptive resedimented volcaniclastic and mixed siliciclastic-volcaniclastic rocks is over 2500 m thick, and at least 1000 m of the overlying deposits have been eroded already. In the northwest of the complex, the oldest proximal zone lithofacies associations overlie basal fossiliferous siltstone, limestone and calcarenite. As the strata, in general, verge toward the southeast, the oldest lavas can be traced over a distance of about 2 km to the east and south although their thickness changes (**Figure 4**). Younger, medial-zone lithofacies associations occur in the east and south and their development is typically complex (**Figures 5** and **6**). The Kramarica Sill is the largest shallow intrusive body in the Smrekovec Volcanic Complex. Its emplacement was related to the formation of a new vent along the Periadriatic Line, some 6 km east of the older one located northwest of Travnik (**Figure 2**).

A detailed study of lithofacies and alteration has been carried out in two sections composed of medial-zone lithofacies associations, namely Krnes and Smrekovec

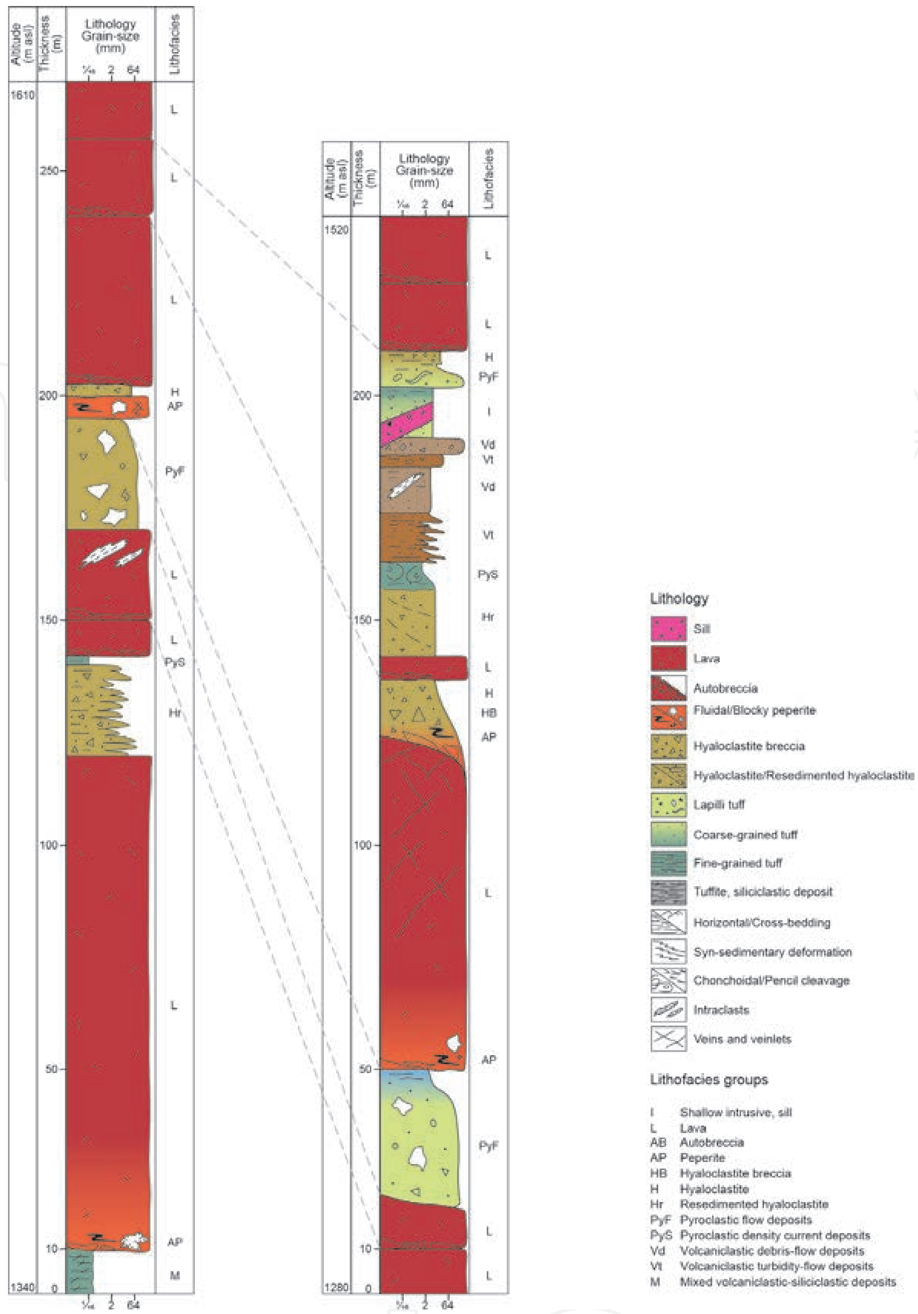

Figure 4.
The sections Presečnik (left) and Javorec (right) situated in the proximal zone show the change in thickness of lithofacies within a distance of 1.5-2 km toward the southeast.

G34, attaining 400 m and 470 m, respectively (**Figures 5** and **6**). The section Krnes consists of complexly alternating pyroclastic, autoclastic and syn-eruptive resedimented volcaniclastic deposits with only two thicker lava flows attaining some 25 m and 70 m. Pyroclastic deposits are dominated by fine-grained cross-bedded and horizontally bedded tuffs related to pyroclastic density currents [36], similar to the occurrences described by [48–51]. Pyroclastic flow deposits [36] are less abundant and commonly consist of basal massive lapilli tuff and the overlaying stratified coarse- and fine-grained tuff. Syn-eruptive resedimented deposits are abundant and comprise volcaniclastic debris-flow deposits and volcaniclastic turbidity flow deposits. Hyaloclastites and resedimented hyaloclastites are subordinate in occurrence but still relatively abundant. Siliciclastic silts are very rare and occur in thin, up to some dm thick stratified units. There are nine peperite deposits occurring at the base and along terminal parts of smaller lava flows.

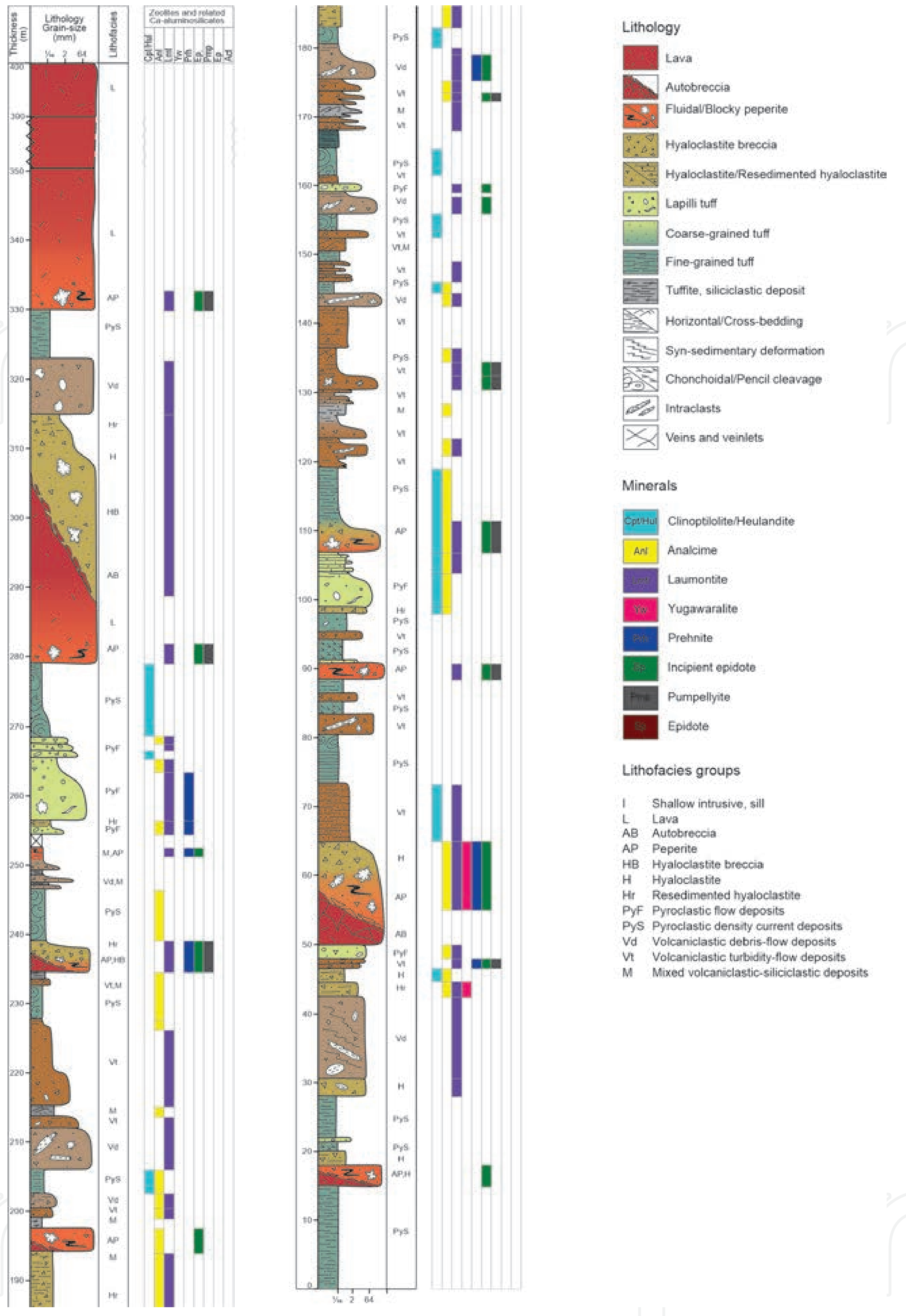

Figure 5.
Lithofacies and the principal alteration minerals in the medial-zone section Krnes.

The section Smrekovec G34 begins in the Kramarica Sill (**Figure 6**) and comprises three thicker lava flows attaining some 35 m, 90 m and over 50 m, respectively. Based on the occurrence of yugawaralite [37, 52] and with respect to the middle bathyal water depths, the Kramarica Sill was emplaced about 600-800 m below the then surface of stratovolcano. Pyroclastic density current deposits are far less abundant than in the section Krnes and pyroclastic flow deposits are relatively abundant only in the upper half of the section. Syn-eruptive resedimented volcaniclastic deposits are dominated by volcaniclastic debris-flow deposits. Hyaloclastites and resedimented hyaloclastites are less abundant than in the section Krnes. Altogether fifteen peperites have been recognised and most of them are related to terminal parts of lava flows.

DOI: http://dx.doi.org/10.5772/intechopen.95480

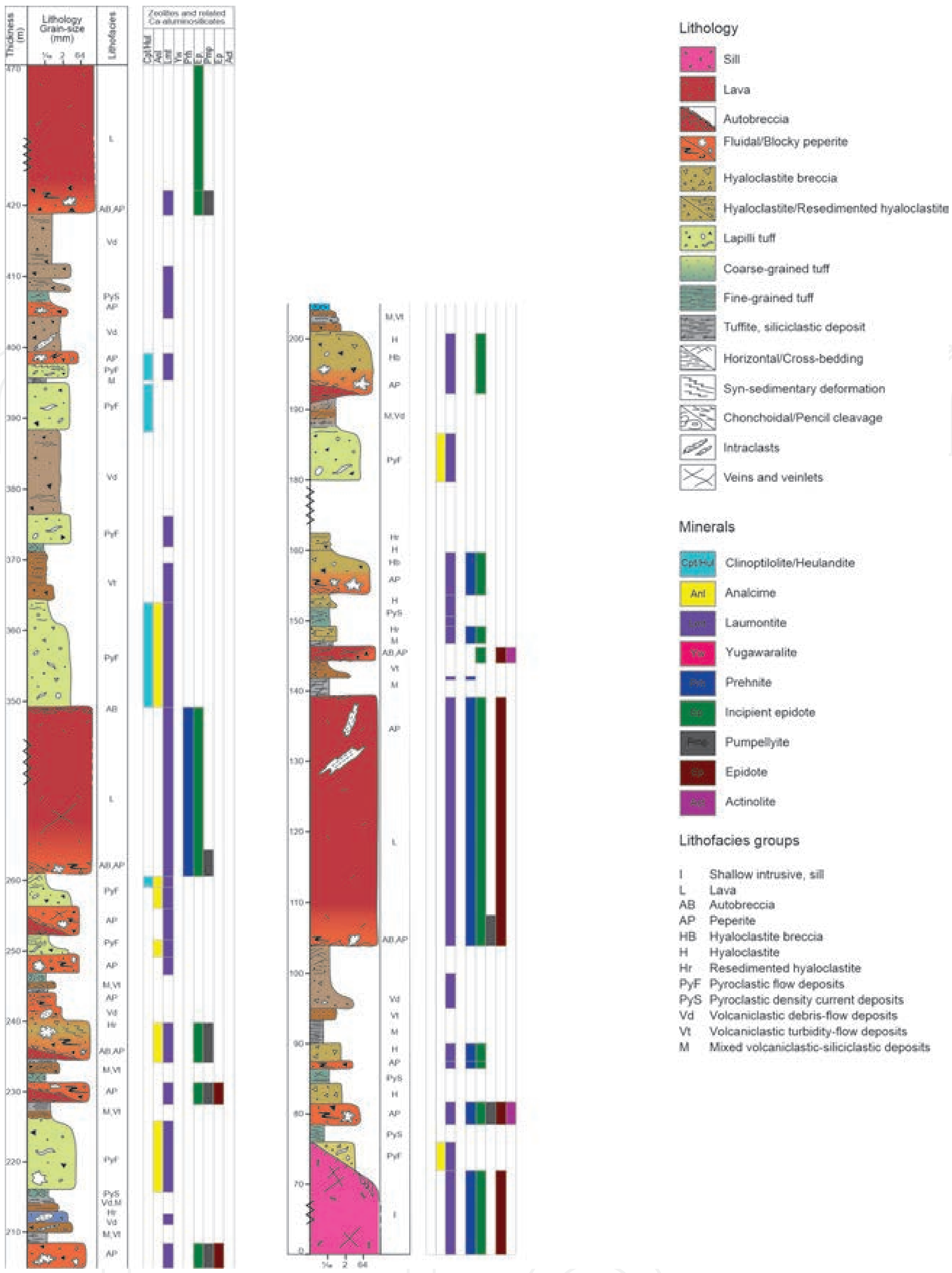

Figure 6.
Lithofacies and the principal alteration minerals in the medial-zone section Smrekovec G34.

4. Occurrence, texture and composition of peperites

In the study area peperites often occur as sheet-like bodies along basal contacts of lava flows and the underlying wet sediments (**Figure 7A, B**). Sometimes they are encountered on the top of thin lava flows burrowing into a several m thick sequence of fine-grained sediments or along terminal parts of lava flows where they form irregularly shaped or lobate bodies. Peperite domains range in volume from less than a few m^3 to several 10s m^3 and sometimes they can only be some cm thick. The mingling wet sediment was commonly fine-grained volcanic ash or siliciclastic and carbonaceous silt. More rarely peperites have been recognised in association with coarser-grained volcaniclastic deposits, and most often they occur at the base of lava flows.

The most widespread type is blocky peperite whilst globular peperite and peperitic hyaloclastite are rarer in occurrence. Along the pathway of a single lava flow overriding the same layer of wet sediment the volume and texture of peperite have commonly changed. On a macroscopic scale, an initiation of peperite development along the contact of lava and fine-grained wet sediment was deformation of the underlying strata and laminae, their disintegration into clasts (**Figure 7A**) and subsequent incorporation into the lava flow where the clasts have undergone further deformation (**Figure 7B**). Terminal parts of lava flows commonly consist of blocky peperite. A clear zonation of closely packed blocky peperite next to lava and dispersed blocky peperite closer the host sediment has not been identified. Most often irregularly distributed domains of the mentioned textural types have been encountered. Some juvenile clasts may be jigsaw-fit and in some peperite domains, a part of the mingling sediment may occur in the form of clasts (**Figure 8A, B**).

Figure 7.
A, disrupted stratified fine-grained tuff underlying hyaloclastite breccia and peperite. The dotted and dashed lines mark a peperite domain (P) and a separated clast composed of disrupted and convoluted stratified tuff (SC), respectively. Hammer (33 cm) is for scale; B, peperite (P) with abundant clasts of dark-grey fine-grained tuff. The dotted lines mark two larger deformed clasts originating from the underlying deposit (T).

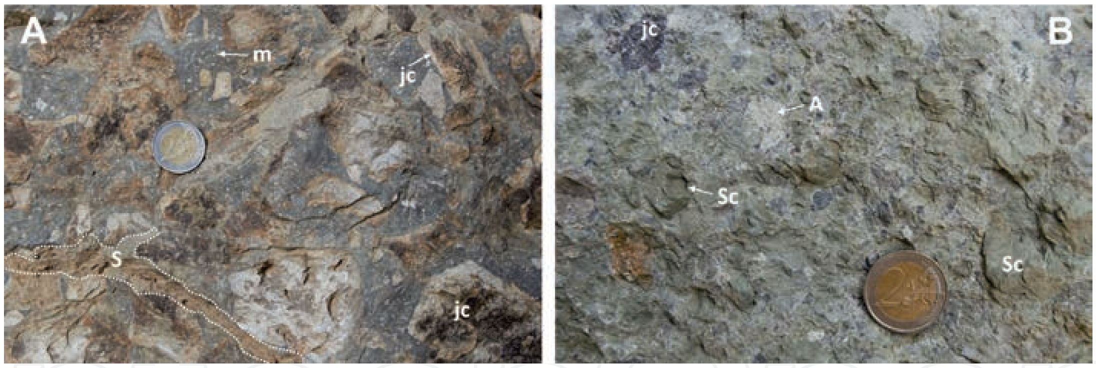

Figure 8.
Blocky peperite. A, larger angular juvenile clasts (jc) and fluidised sediment (S, dotted area) in matrix (m) composed of smaller juvenile clasts and fine-grained siliciclastic sediment. Coin (2.5 cm) is for scale; B, juvenile clasts (jc) and the clasts of fine-grained tuff (Sc) in matrix composed of an intimate mixture of the host sediment and juvenile clasts. The matrix is locally extensively altered (A) to laumontite. Coin (2.5 cm) is for scale.

On a macroscopic scale, blocky, sharply angular juvenile clasts are the most common (**Figure 9A**) although other forms of juvenile clasts have been recognised as well (**Figure 9B**-**F**). Globular juvenile clasts can be irregularly shaped or amoeboid (**Figure 9B, C**), elongated, tapered, and a single clast can have partially fluidal and sub-planar margins. Mixed morphologies of juvenile clasts, particularly sharply angular and elongate globular have been encountered in some rhyodacitic glassy lava flows (**Figure 9E**). Glassy lavas sometimes undergo ductile fragmentation into irregularly shaped elongated and convoluted globular clasts that resemble welded glass-shards (**Figure 9F**). Intergranular space is relatively limited and poorly interconnected, and can be infilled with very fine-grained, possibly suspended sediment. Further disintegration and mingling with wet sediment produced peperites developed as intimate mixtures of both components.

The host sediment can penetrate magma in the form of curviplanar and vermicular indentations or enter lava flow through laminar boundary layers. The indentations (**Figure 10A**) reaching deeper into the juvenile clasts are commonly disconnected (**Figure 10B, C**) and initially, irregularly shaped droplets formed (**Figure 10D**). The droplets commonly advanced deeper into juvenile clasts changing their shapes into spherical and oval (**Figure 10E, F**). They may be very abundant, and the rock can be termed microglobular peperite, similar to that described by [5]. In an advanced stage peperites of this type may evolve into intimate mixtures of extremely irregularly shaped elongated clasts and tongues of sediment and tapered juvenile clasts having tendril and wispy forms (**Figure 11A**). The host sediment that penetrates lava through laminar boundary layers at least initially follows the laminae adopting their shape (**Figure 11B**), but then the flow with the admixed sediment seems to have changed into turbulent (**Figure 11C**). Sometimes the amount of sediment that mingled with magma in that manner is very low and only isolated patches of the entrained sediment can be encountered in the predominant magma, but there are cases where peperites locally developed as intimate mixtures of nearly equal proportions of tapered juvenile clasts and deformed, elongated clasts of sediment (**Figure 11D**).

Magma can penetrate the adjacent sediments forming platy or tapered juvenile clasts (**Figure 11E**). Magma can also penetrate the host sediment along the strata boundaries or other disconformities related to syn-sedimentary tectonic activity or erosion. The emplacement of the Kramarica Sill also disrupted partially consolidated and unconsolidated sediments and made pathways for magma penetration (**Figure 11F**).

When the unconsolidated mingling sediment is composed of coarse-grained volcaniclastic deposit such as volcaniclastic turbidite or debris flow deposit,

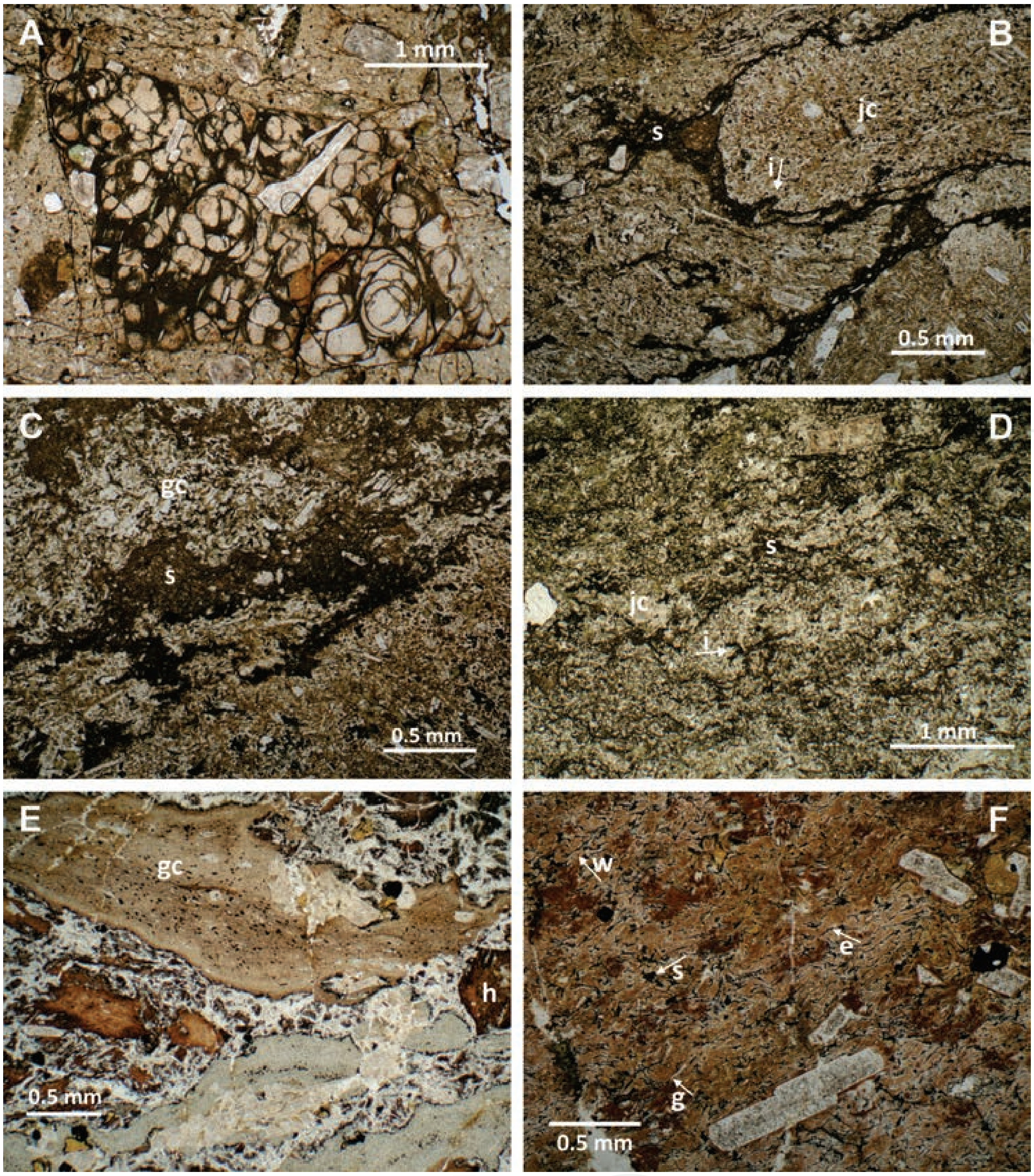

Figure 9.
(A) angular juvenile clast with perlitic cracks in siliciclastic host sediment. Volcanic glass in perlitic domains is altered to laumontite (white) and Fe-oxides (black); (B) various shapes of juvenile clasts (jc) with indentations (i) of the host sediment (s); (C) amoeboid juvenile clasts (gc) in the host sediment (s); (D) an intimate mixture of juvenile clasts (jc) with the sediment (s) indentations (i), (E) globular(gc) and angular (h) juvenile clasts; (F) a glassy lava fragmented into globular (g), elongated (e) and convoluted (w) juvenile clasts with altered sediment (s) filling interstitial space.

peperites can form by erosion and incorporation of sediment into the lava flow. A small-scale penetration of magma into interstitial space has been observed along the basal contacts of lava flows and the underlying sediments (**Figure 12A**). Sometimes magma penetrated deeper into the sediment while pushing aside and redistributing its constituents such as mineral grains and volcanic rock fragments (**Figure 12B**), although the advance seems very limited as the penetrating tongues soon became thinner (**Figure 12C**) or have been stopped by an impenetrable obstacle. Magma itself possibly underwent a sort of separation of its constituents during the process of penetration. Phenocrysts are often stacked close to the magma-sediment boundary while glassy groundmass could have penetrated deeper into the sediment (**Figure 12D**).

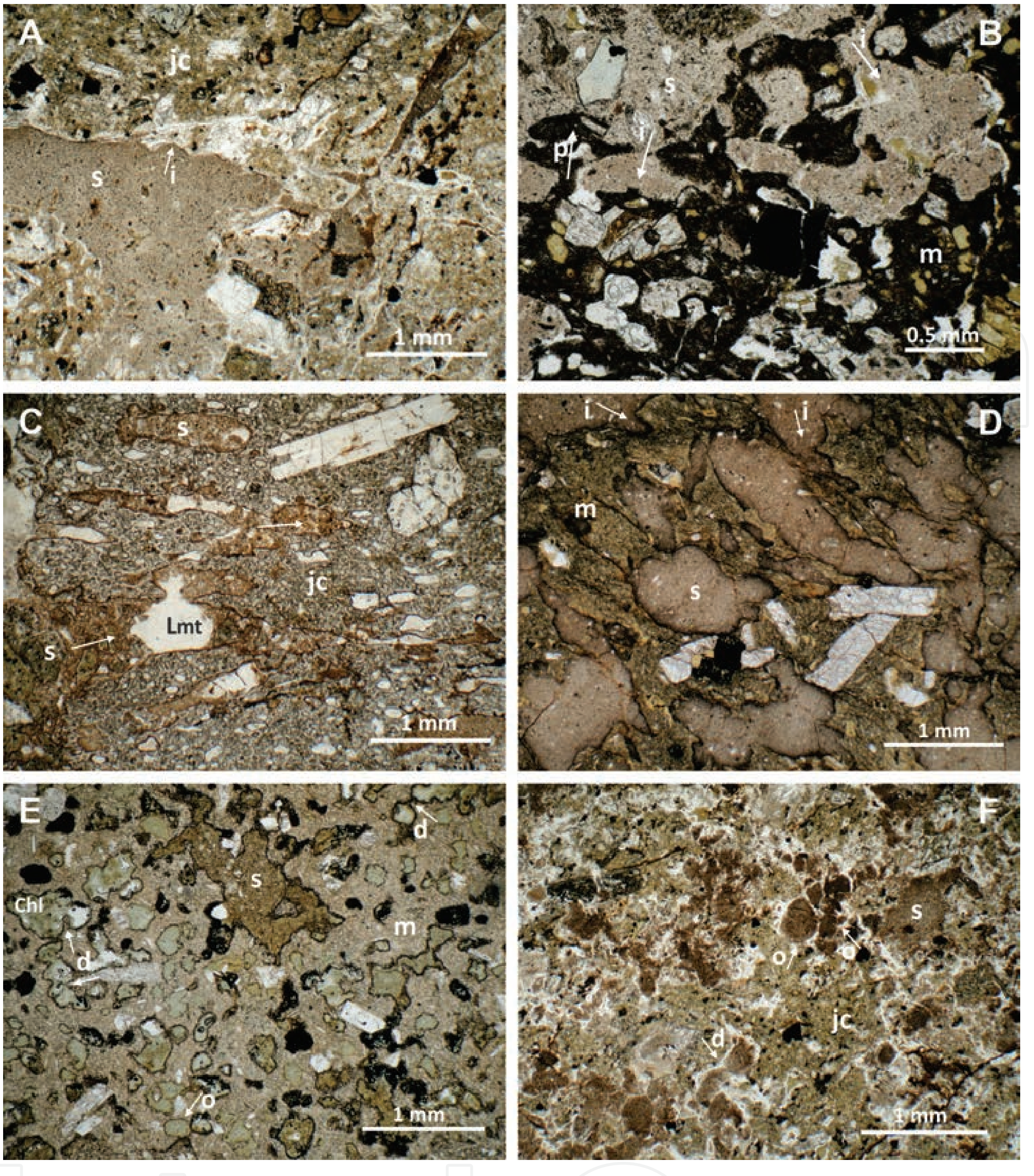

Figure 10.
(A) curviplanar indentations (i) of sediment (s) into juvenile clasts (jc); (B) interpenetrating sediment (s) and magma (m). The arrows i and p indicate the penetration directions of sediment and magma, respectively; (C) sediment (s) penetrating juvenile clast (jc). The arrows show the sediment penetration directions. Sediment (brownish) is partially unaltered and partially replaced by laumontite (Lmt). Larger detached droplets of sediment have irregular shapes whilst smaller ones tend to develop more oval or spherical shapes; (D) irregularly shaped droplets of sediment (s) penetrating a juvenile clast (m). The arrows (i) show the sediment penetration directions; (E) larger clast of sediment (s) penetrating a juvenile clast (m) is still unaltered, and smaller ones have already undergone alteration into chlorite (Chl). Some droplets of sediment show the tendency of splitting into several smaller droplets (d) and some smaller droplets already attained oval shapes (o); (F) droplets of siliciclastic sediment (s) in a juvenile clast (jc). Some droplets have oval shape (o) and some droplets indicate their shapes evolved by splitting of larger clasts (d).

5. Alteration of peperites

Microfacies of peperites has been an essential tool in recognition of alteration of peperites as it encompasses the change in mineral and chemical composition of juvenile clasts and the mingling sediment, and more rarely, the formation of interstitial cement. Juvenile blocky clasts dispersed in abundant siliciclastic silt commonly underwent only devitrification, the alteration of glassy juvenile clasts with perlitic

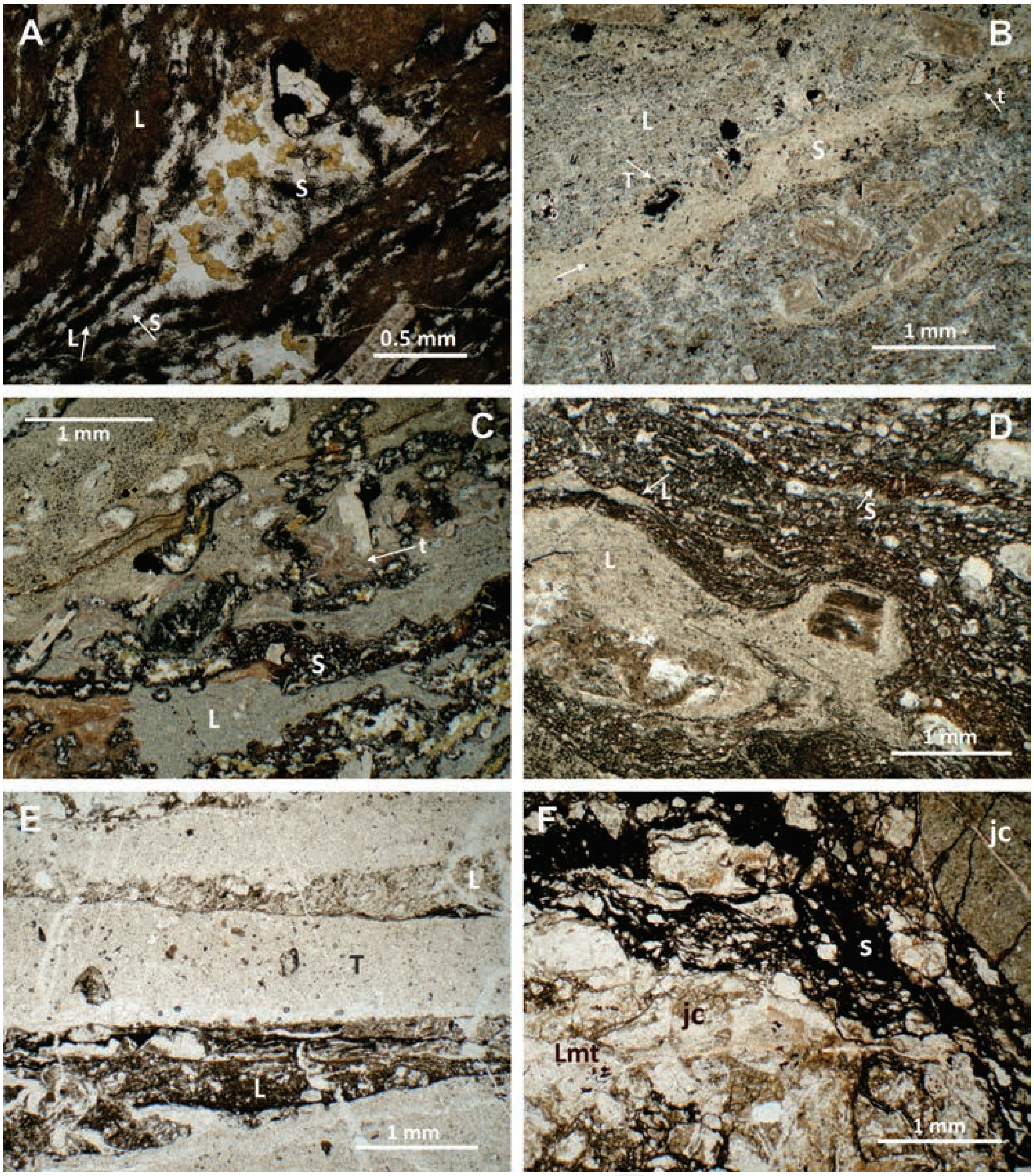

Figure 11.
(A) an intimate mixture of elongate altered clasts of sediment (S) and juvenile clasts (L); (B) sediment (S) entrained into lava flow (L) through a laminar boundary layer. The arrow shows the entrainment direction. The elongated sediment clast soon becomes thinner (t). Along the first obstacle it becomes thicker (T) by enclosing the phenocryst, and then becomes thinner by avoiding the second phenocryst; (C) microstructure of peperite indicating turbulent flow (t) by disrupted and convoluted sediment layers (S) in lava (L); (D) an intimate mixture of elongated clasts of sediment (S) and juvenile clasts (L); (E) platy juvenile clasts (L) formed by penetration of magma into fine-grained volcanic ash (T); (F) juvenile clasts (jc) and fluidised sediment (S) developed owing to the intrusion of the Kramarica Sill. The sediment is altered to iron oxides and the larger juvenile clast to laumontite (Lmt).

cracks may involve the formation of laumontite and Fe-oxides (**Figure 9A**). The mingling sediment is, in general, unaltered except for locally developed iron oxides.

Peperites with denser population of juvenile clasts, and particularly juvenile clasts having irregular fluidal or amoeboid shape, that mingled with siliciclastic silt are commonly altered to laumontite or laumontite and iron oxides. The host sediment commonly remained unaltered (**Figure 13A**).

Some juvenile clasts are replaced by the assemblage of laumontite, albite, quartz, actinolite and epidote (**Figure 13B**), or laumontite, albite, quartz, pumpellyite, incipient epidote and chlorite, or laumontite, prehnite, quartz, chlorite and

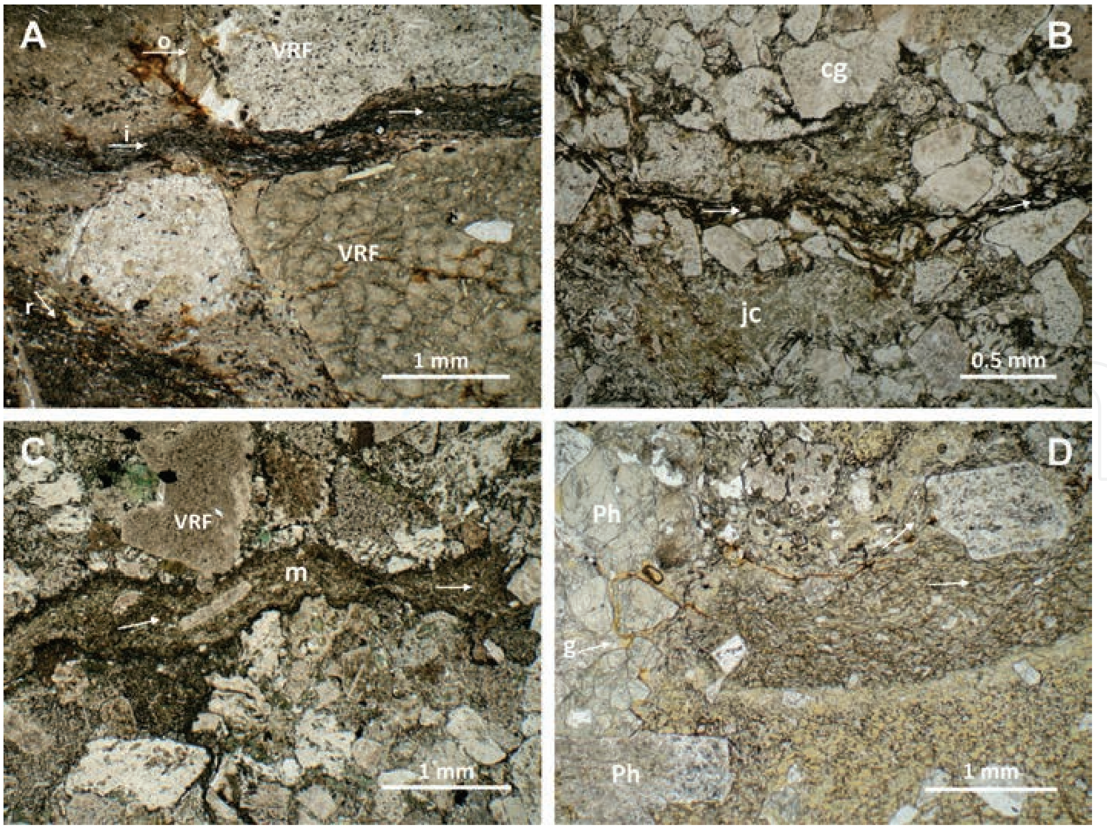

Figure 12.
(A) the arrows (i) and (r) show the directions of magma penetration in intergranular space of volcaniclastic turbidite deposit. The arrow (o) indicates the cessation of penetration along a volcanic rock fragment (VRF); (B) penetration of magma (arrows) into volcaniclastic turbidite deposit by pushing aside crystal grains (cg). The cessation of penetration resulted in the formation of a juvenile clast (jc); (C) penetration of magma (m) stopped by crystal grains, the direction is marked by arrows, VRF – volcanic rock fragments; (D) stacked phenocrysts (Ph) of augite and a glassy constituent of magma (g) that penetrated somewhat further into volcaniclastic turbidite deposit, the arrows mark the directions of magma penetration.

incipient epidote, or laumontite, analcime and interlayered chlorite-smectite. Incipient epidote [53] refers to some μm to a few 10 μm sized, oval and highly birefringent grains. If the mingling sediment was siliciclastic silt it is often altered to microcrystalline quartz, incipient epidote and iron oxides.

If the mingling sediment was fine-grained pyroclastic deposit the alteration minerals commonly resemble those in the juvenile clasts. The most extensive alteration underwent the clasts composed of fine-grained pyroclastic deposit that were incorporated into lava flow, or fine-grained pyroclastic sediment that was entrained into lava flow through lamination boundary layers (**Figure 13C**). A common alteration assemblage is albite, prehnite, quartz, iron oxides and chlorite or interlayered chlorite-smectite with more than 80% of chlorite layers [54]. In the advanced stage of mingling (**Figure 11A**) the alteration of sediment commonly remained the same while the juvenile clasts can be altered to iron oxides and chlorite.

Penetration of the host sediment into juvenile clasts had immediate impact to its alteration. Before the sediment penetrated juvenile clasts and also in the initial stage of formation of droplets it commonly remained unaltered (**Figure 10B,C**), but with advanced penetration and subsequent dispersion into the juvenile clasts, and the transformation of shape from irregular to spherical and oval, the alteration advanced as well (**Figure 10E, 13D**). Such inclusions of the host sediment closely resemble vesicle fillings and could be easily misinterpreted. Common alteration minerals are laumontite (**Figure 13D**), and the assemblages of or prehnite, laumontite and quartz (**Figure 13E**), or pumpellyite, albite, quartz and chlorite (**Figure 13F**), or laumontite, prehnite, quartz, epidote and chlorite.

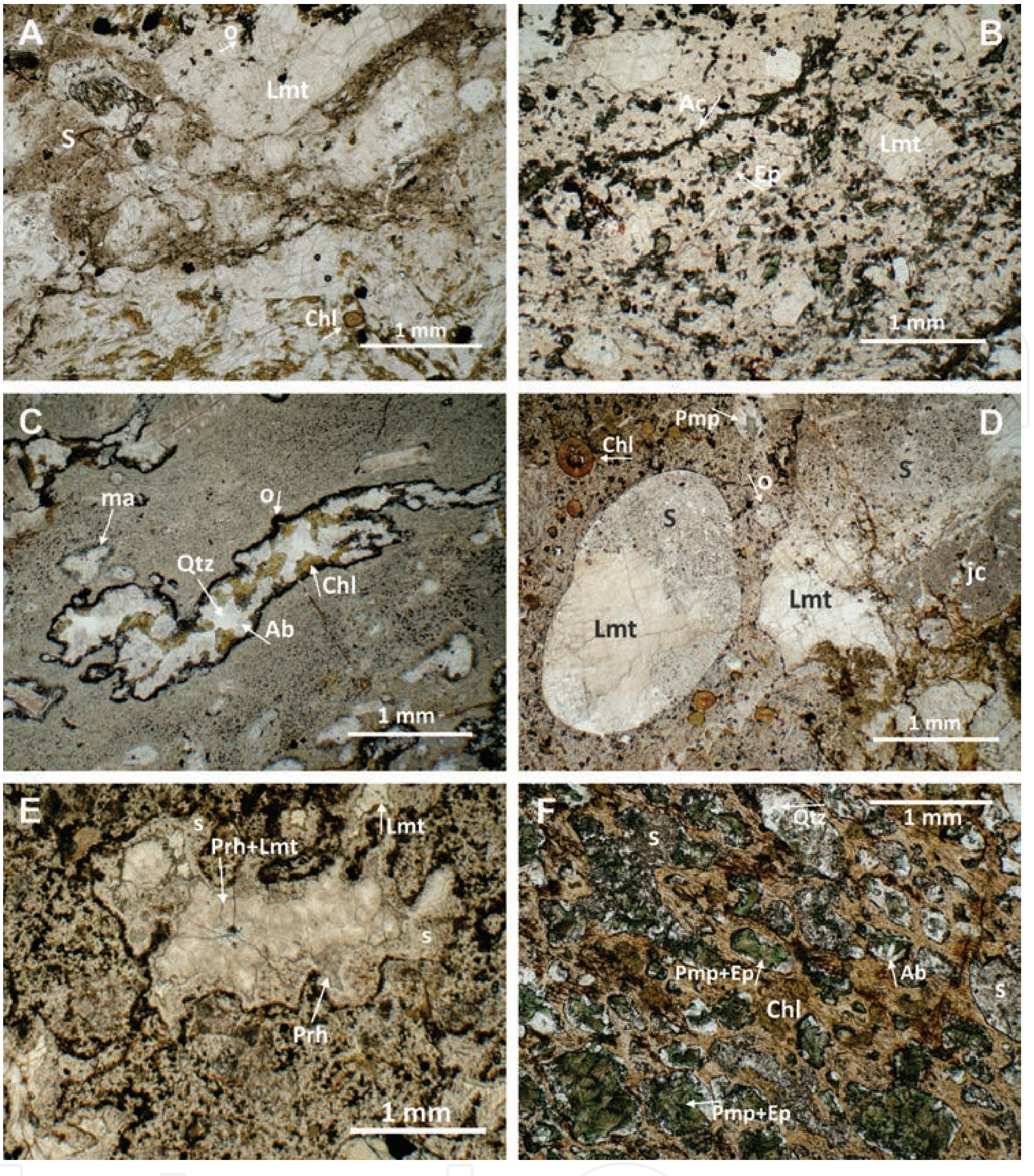

Figure 13.
(A) juvenile clasts (white) altered to laumontite (Lmt), iron oxides (o) and chlorite (Chl). The composition of the mingling siliciclastic sediment (S) remained largely unaltered; (B) a juvenile clast altered to laumontite (Lmt), epidote (Ep) and actinolite (Ac); (C) a clast of fine-grained pyroclastic deposit incorporated in a lava flow has been altered to albite (Ab), quartz (Qtz), chlorite (Chl) and Fe-oxides (o). Some clasts underwent magma assimilation (ma); (D) the mingling fine-grained pyroclastic deposit (S) formed a large oval inclusion in a juvenile clast that has been partially altered into laumontite (Lmt). Smaller inclusions are altered to pumpellyite (Pmp) and quartz, some small spherical inclusions are unaltered (o) and the other replaced by chlorite (Chl). juvenile clasts (jc); (E) an inclusion of fine-grained pyroclastic deposit (s) in a juvenile clast altered to prehnite (Prh) and laumontite (Lmt); (F) inclusions of fine-grained pyroclastic deposit in a juvenile fragment (brownish) altered to pumpellyite (Pmp), epidote (Ep), quartz (Qtz) and albite (Ab). Volcanic glass in the juvenile clast is locally replaced by chlorite (Chl).

Platy juvenile clasts related to penetration of magma into the host sediment are commonly extensively altered into laumontite and iron oxides (**Figure 11E**). The same assemblage typically replaces irregularly shaped juvenile clasts in peperites formed during the emplacement of the Krmarica Sill (**Figure 11F**).

The alteration of peperites related to coarse-grained host sediment is characterised by chlorite, interlayered chlorite-smectite with more than 90% of chlorite layers, quartz, and sometimes incipient epidote. Laumontite and other zeolites, and pumpellyite, prehnite and epidote are uncommon (**Figure 12A-D**).

6. Peperite alteration in the succession of volcanic deposits and the stratovolcano-hosted hydrothermal system in the Smrekovec Volcanic Complex

The stratovolcano-hosted hydrothermal system with convective-advective flow regime of hydrothermal fluids (**Figure 3**), and another important event in the evolution of hydrothermal alteration of volcanic deposits was the emplacement of the Kramarica Sill. Consequently, volcanic deposits underwent alteration related to diverse processes and different superimposed stages of hydrothermal activity [37].

The largest source of geothermal energy and hydrothermal fluids in the time span of volcanic activity some 28-23 mya [43] was a deep igneous body. The alteration resulting from an elevated geothermal gradient is characterised by clinoptilolite, heulandite, analcime, smectite and interstratified smectite-chlorite. The convective flow of hydrothermal fluids occurred primarily through fracture systems and the most typical mineral formed owing to hydrothermal activity is laumontite. Where the fractures were densely distributed, the adjacent rock was altered as well. Laumontite occurs as interstitial cement and replaces volcanic glass and intermediate plagioclases in assemblage with albite, and the principal phyllosilicate mineral is chlorite or interstratified chlorite-smectite with over 80% of chlorite layers. Advective outflow of hydrothermal fluids preferentially occurred through high-permeability layers of the stratovolcano edifice, and laumontite, chlorite, albite and more rarely prehnite are typical minerals encountered in coarse-grained rocks such as volcaniclastic breccias. The adjacent, lower-permeability layers contain authigenic minerals with lower temperature stability ranges, namely clinoptilolite, heulandite, analcime and interlayered chlorite-smectite (**Figures 5** and **6**) [37, 38]. Stilbite locally occurs as vein mineral and was developed during late-stage of hydrothermal activity.

The emplacement of the Kramarica Sill (**Figure 2**) was related to the formation of new vent along the Periadriatic Line. Thermal effects of the emplacement promoted a number of progressive alteration reactions such as from laumontite to prehnite, laumontite to yugawaralite, or interlayered chlorite-smectite to chlorite. During the cooling of the sill, local hydrothermal conditions persisted and controlled retrograde reactions such as from prehnite to yugawaralite, from prehnite to laumontite, from laumontite to heulandite or analcime and from chlorite to interlayered corrensite-chlorite [37, 38, 54].

7. Discussion

The formation of alteration minerals in volcanic-hydrothermal systems is a complex process affected by temperature, pressure, composition of reacting fluids, porosity, permeability and initial composition of the host-rock, duration of hydrothermal activity and superimposed thermal (or hydrothermal) regimes [55, 56]. Nevertheless, there is a general relationship between temperature and the formation of alteration minerals, and some mineral assemblages can be used to interpret temperatures within a geothermal system (**Figure 14**). For heulandite and stilbite, laumontite, yugawaralite, pumpellyite and actinolite widely accepted temperature stability ranges are 100-120°C, 120-220°C, 172-234°C, 200-310°C, 220-310°C and 280-460°C [52, 55–65]. Incipient, fine-grained and poorly crystallised epidote has been encountered in hydrothermal systems of the Philippines [53, 55] and the Nisyros Island [63], respectively, in the temperature range of 180-220°C although epidote generally forms at temperatures higher than 240°C [64, 65]. The temperature stability range of 245-265°C has been reported for mixed-layer R0 and R1 chlorite-smectite from Nesjavellir geothermal field, Iceland [66].

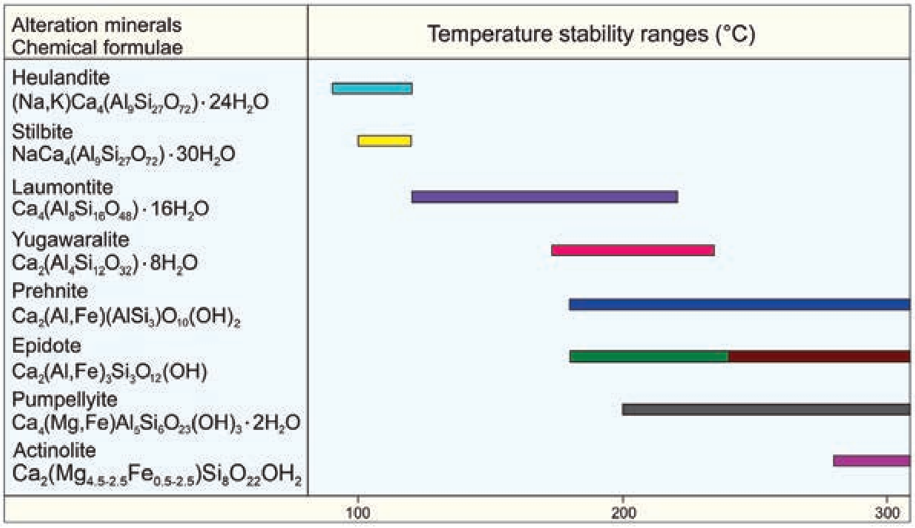

Figure 14.
Authigenic calcium-aluminosilicate minerals that commonly serve as geothermometers in volcanic-hydrothermal systems, their chemical formulae and temperature stability ranges, compiled from [52, 55–65].

The alteration of peperites from the Smrekovec Volcanic Complex indicates close relationship to the rock composition and texture, and therefore, the style of peperite formation. Porosity and permeability of peperites is, in general, lower than that of the host sediment. The types involving fine-grained host sediments have low permeability and low porosity, and in the stratovolcano-hosted hydrothermal system with convective-advective flow regime (**Figure 3**) they must have functioned as aquicludes unable to drain effectively the advective flow of hydrothermal fluids that largely controlled hydrothermal alteration of volcanic deposits [37]. In such hydrothermal system, peperites involving coarse-grained host sediments should be more extensively altered and contained authigenic minerals with higher temperature stability ranges than the types involving fine-grained host-sediments, but that is not the case. On contrary, in this type of peperites significant authigenic calcium-aluminosilicate minerals are often lacking and the most common alteration mineral is chlorite or interlayered chlorite-smectite.

In dispersed blocky peperite, matrix composed of siliciclastic host sediment is usually unaltered. The alteration of juvenile clasts often indicates only the reactions of devitrification of volcanic glass, and only juvenile clasts with perlitic cracks can be altered to laumontite and Fe-oxides (**Figure 9A**). The activity of hot fluids originating from heated pore waters can be assumed, but chemical gradients favourable for the formation of laumontite were attained only inside the juvenile clasts with perlitic cracks. Perlitic cracks apparently served as conduits for hot fluids that leached volcanic glass during the flow, and in this manner underwent the changes in chemical composition (e.g. [67]) that finally resulted in crystallisation of laumontite. Far more extensive alteration of blocky peperites involving fine-grained pyroclastic host sediment supports the forementioned explanation. The interaction of heated pore fluids and highly reactive host sediment apparently controlled geochemical evolution of so-formed hydrothermal solutions and the related extensive alteration of all constituents of peperite. Laumontite or mineral assemblages of laumontite, albite, quartz, pumpellyite, incipient epidote and chlorite, or laumontite, prehnite, quartz, chlorite and incipient epidote, or laumontite, analcime and interlayered chlorite-smectite indicate that temperature gradients were prerequisite but not sufficient for alteration to occur and that the main controlling factor were geochemical gradients.

Microglobular peperite has been interpreted as a frozen example of a fuel-coolant interaction (FCI) between magma and fluidised host sediment [5], and the temperatures of alteration reactions in direct contact with magma must have been higher than in blocky peperite. Microglobules of fine-grained pyroclastic sediment underwent alteration, and typically, smaller microglobules are commonly completely altered to authigenic mineral assemblages with higher temperature stability ranges (e.g. pumpellyite, epidote) than the larger ones that remained incompletely altered or altered to authigenic minerals with lower temperature stability ranges (e.g. laumontite) (**Figure 13D**). The relationship indicates that high-temperature conditions could not persist for a long period of time.

Despite of the complexity of alteration of volcanic deposits in lithofacies associations of the sections Krnes and Smrekovec G34 the assemblages of authigenic minerals in peperites are different than those in the adjacent underlying and overlying autoclastic, pyroclastic or resedimented volcaniclastic deposits irrespectively of their texture and grain-size (**Figures 4** and **5**). Particularly outstanding is the occurrence of pumpellyite, actinolite and epidote. In lavas pumpellyite and actinolite very rarely occur as the replacement of volcanic glass and other primary constituents although the temperatures in cooling lavas could be favourable for their formation.

If compared to the section Krnes, the alteration of volcanic deposits in the section Smrekovec G34 has been far more complex owing to the emplacement of the Kramarica Sill. Progressive reactions related to an elevated temperature regime are characterised by the occurrence of prehnite and indicate, at least in the lower half of the section, that the temperatures could have reached over 300°C. Yet, even in such elevated temperature regime the exclusive occurrence of pumpellyite and particularly actinolite in peperites indicates that higher temperatures and specific geochemical conditions related to the formation of peperites must have controlled the crystallisation of pumpellyite and actinolite. The occurrence of the same assemblage in peperites in the section Krnes is particularly important. Here, hydrothermal activity and temperature regime were mainly related to a deep igneous source and the associated convective-advective flow of hydrothermal fluids and elevated geothermal gradients in the area of stratovolcano, and they were not affected, at least significantly, by the emplacement and cooling of the Kramarica Sill. Maximum temperatures have been determined by the temperature stability of laumontite, namely, 234°C which is insufficient for the crystallisation of pumpellyite or actinolite. The alteration of juvenile clasts to laumontite in peperites indicates the presence of hydrothermal conditions although they cannot be conclusively ascribed to specific hydrothermal conditions and geochemical gradients related to the formation of peperites.

The alteration of peperites can be regarded as syn-formational hydrothermal, although it is local, specific and ephemeral lasting until thermal gradients persisted. Authigenic mineral assemblages developed in peperites from the Smrekovec Volcanic Complex are rare on a worldwide scale and have not been identified in such context yet. Geochemical evolution of heated pore fluids circulating in the vicinity of the source of heat controlled the formation of authigenic mineral assemblages and the presence of unstable, reactive volcanic material was crucial for their formation and diversity.

8. Conclusion

Peperites are commonly developed in submarine environments with contemporaneous volcanic activity and sedimentation. And although the occurrence and complex processes of formation have been studied and explained in many modern and ancient geological settings worldwide [4, 10–14], and particularly in the

Carpathian-Pannonian region [9, 15–17] where the Smrekovec Volcanic Complex belongs to [29], the studies related to their alteration have been relatively scarce [15–20]. The present study gives evidence of the existence of localised and ephemeral hydrothermal conditions related to and persisting during the formation of peperites and resulting in their distinct alteration.

The Smrekovec Volcanic Complex is a remnant of an Oligocene submarine stratovolcano characterised by a complex development of an over 2500 m thick succession of volcanic rocks. Submarine environment, the style of eruptions, morphology and the abundance of pyroclastic and syn-eruptively resedimented volcaniclastic deposits were favourable for the formation of peperites that are particularly abundant in medial-zone lithofacies associations. In a succession of volcanic deposits studied in detail in two sections Krnes and Smrekovec G34 attaining 400 m and 470 m, respectively, the alteration of peperites indicates that authigenic minerals have higher temperature stability ranges than those in the adjacent underlying and overlying deposits irrespectively of their lithofacies.

The alteration of peperites indicates close relationship to the rock composition and texture, and therefore, the style of peperite formation. Dispersed blocky peperite involving siliciclastic host sediment is commonly poorly altered. Volcanic glass in juvenile clasts is usually devitrified or hydrated, and only some clasts with perlitic texture can be altered to laumontite. In the textural types with fine-grained pyroclastic host sediment laumontite, or the assemblages of laumontite, albite, quartz, pumpellyite, incipient epidote and chlorite, or laumontite, prehnite, quartz, chlorite and incipient epidote, or laumontite, analcime and interlayered chlorite-smectite may occur. The alteration minerals indicate that thermal gradients were prerequisite but not sufficient for alteration to occur and that the main controlling factor were geochemical gradients in reacting fluids.

Microglobular peperite developed by interaction between magma and fluidised sediment [5], and the temperatures of alteration must have been higher than in blocky peperite. Smaller microglobules are often completely altered to authigenic mineral assemblages with higher temperature stability ranges (e.g. pumpellyite, epidote) while the larger microglobules remained incompletely altered or altered to authigenic minerals with lower temperature stability ranges (e.g. laumontite). The relationship indicates that high-temperature conditions could not persist for a long period of time and had ephemeral character.

Authigenic mineral assemblages developed in peperites indicate that their formation is specific and related to the formation of parent rock itself. Thermal stability ranges of actinolite and pumpellyite indicate the highest temperatures possibly exceeded 280°C and decreased when the parent lava flow and the associated peperite underwent cooling. Hydrothermal fluids mainly originated from heated pore fluids although deuteric fluids could have been locally admixed. The evolution of fluids circulating in peperite was essential for extensive alteration to occur and that was possibly attained by interaction with unstable and highly reactive host sediment. Many peperites have been developed as low-porosity and low-permeability layers, and therefore contemporaneous and later hydrothermal activity related to the stratovolcano-hosted hydrothermal system with convective-advective flow could not have exerted any critical thermal or geochemical impact.

The alteration of peperites in the Smrekovec Volcanic Complex can be regarded as syn-formational, hydrothermal, ephemeral, localised and depending on many factors such as the extent and time span of thermal regime, the process of formation of parent rock and thermal and geochemical evolution of circulating hydrothermal fluids. And although peperite deposits are not rare in similar volcanic-sedimentary settings worldwide, the alteration as recognised in the present study has not been reported yet and indicates the formation and alteration of peperites are complex and distinctive and interrelated processes.

Acknowledgements

Slovenian Research Agency (ARRS) is acknowledged for granting the research (Programme Mineral Resources P-0025). The editorial work of Academic Editor Dr. Károly Németh and helpful comments of anonymous reviewers are greatly appreciated. Many thanks to Mrs. Mia Vulovic, Author Service Manager for her kind assistance. I thank Ms. Staška Čertalič and Mr. Mladen Štumergar from Geological Survey of Slovenia for technical support.

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