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# Pumpellyite-prehnite mineral assemblage in Tatric basement and its relation to the Central Western Carpathian units

MARTIN KOVÁČIK

State Geological Institute of Dionýz Štúr, Mlynská dolina 1, SK-817 04 Bratislava;
mato.kovacik@geology.sk

**Abstract**

Pumpellyite ± prehnite-bearing secondary mineral assemblage has been found in several basement rocks of the Tatric Unit. Quartz-free rocks, ranging from amphibolic schists to calc-silicate hornfelses, represent the most appropriate lithology for the pumpellyite forming reactions. Growth and composition of pumpellyite are widely influenced by the type of mineral precursor and fluid infiltration. Besides of tiny veinlets, pumpellyite formed predominantly at the expense of pre-Mesozoic diopside, amphibole, biotite, garnet and fine-grained groundmass. Prehnite replaced mainly An-rich plagioclase. Pumpellyite is represented mostly by Al-type; pumpellyite-(Mg) or lower thermal pumpellyite-(Fe) developed only locally. Based on investigated mineral assemblages and chlorite geothermometric estimations, metamorphic overprint in the Tatric basement-rocks is constrained by pumpellyite-prehnite facies conditions. Alpine tectono-metamorphism is preferred as the main forming process of studied mineral assemblages. The Hronic Unit is envisaged as integral nappe-unit involved in the Alpine (Cretaceous) collision tectonics of the Central Western Carpathians. Based on pumpellyite and/or actinolite occurrences, there is outlined a tentative zonation of the Alpine metamorphism in the Central Western Carpathians.

**Key words:** pumpellyite-prehnite, chlorite geothermometry, Alpine metamorphism, Tatric basement, Hronic Unit, Central Western Carpathians

## Introduction

Pumpellyite and occasionally prehnite were locally identified during regional petrographical investigation of the Tatric metamorphic basement. Presented study is dealing with mineral assemblages being verified by means of electron microprobe, because of their very fine crystal size. It is aimed to provide basic knowledge about genesis, metamorphic conditions and microstructural setting of pumpellyite and prehnite. To wider tectonic assumptions there were involved actual data of the pumpellyite ± prehnite occurrences in the Central Western Carpathians, including the traditional distribution in the Hronic nappe-unit.

## General data on pumpellyite stability

Ideal pumpellyite formulae is given as $Ca_2Al_2(Al,Fe^{3+},Fe^{2+},Mg)[Si_2(O,OH)_7][SiO_4](OH,O)_3$, where the presence of $[Si_2(O,OH)_7]$ expresses whole or partial replacement of oxygens by OH ions (Deer et al., 1992). Pumpellyite-bearing mineral assemblage occurs in a wide range of rocks, namely with contribution of intermediate to basic magmatic source material.

Pumpellyite and specifically pumpellyite-prehnite mineral assemblage belongs to diagnostic petrologic tool of subgreenschist ("anchizonal") metamorphic facies. Upper stability field of pumpellyite is bordered at 250–350 °C at 3–8 kb pressure condition (Frey et al., 1991). Maximum extension of prehnite-pumpellyite subfacies outlines the field between 175 and 280 °C (in 0.5–4.5 kb pressure range) and the pressure stability boundary between pumpellyite and prehnite is situated at about 2–3 kb (Frey et al., 1991). Higher pressure character of pumpellyite, in comparison with prehnite is generally accepted, even though the precise pressure determination is understood poorly. Replacement of pumpellyite by actinolite/tremolite expresses the onset of greenschist facies metamorphism. There were certain relationships observed between the pumpellyite composition and the metamorphic degree: in zeolite subfacies pumpellyite-(Fe) dominates and Al-content (Coombs et al., 1976) as well as Mg-content (Day and Springer, 2005) in pumpellyite rise up with the temperature increase. We may conclude, that according to other thermodynamic calculations (e. g. Powell et al., 1993) or by means of direct measurements in natural geothermal fields (Ewarts and Schiffman, 1983) the pumpellyite-(Fe) is stable also under pressures bellow 1 kb. In some active geothermal fields pumpellyite Fe-member is stable already at 130 °C (Sigvaldason, 1962).

## Geological setting and previous works

From among various tectonic divisions of the Western Carpathians (Fig. 1) the simplified scheme of Mišík et al.

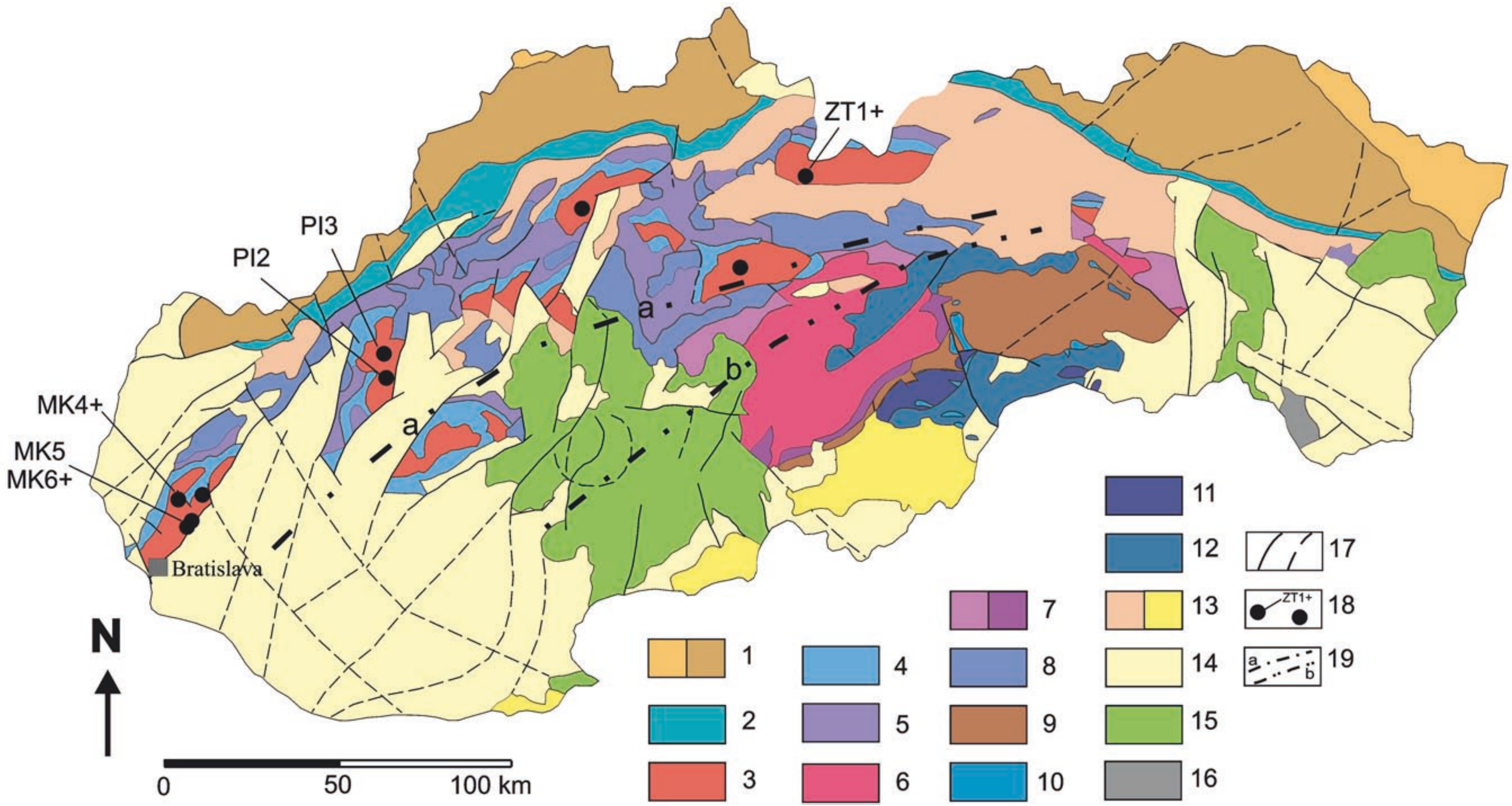



**Fig. 1.** Tectonic sketch of the Slovak part of Western Carpathians (Mišík et al., 1985, adapted). 1 – Flysch belt – Krosno/Magura zone; 2 – Klippen belt; 3 – Tatric basement; 4 – Tatric cover units; 5 – Fatrikum; 6 – Veporic basement; 7 – North/South Veporic cover units; 8 – Hronic Unit; 9 – Gemeric Unit; 10 – Meliatic Unit; 11 – Turnaic Unit; 12 – Silicic Unit; 13 – Inner Carpathian Paleogene/Buda basin; 14 – Neogene basins; 15 – Neogene volcanics; 16 – Zemplinic Unit; 17 – main faults; 18 – samples with identified pumpellyite in Tatric basement (labelled circles – new determinations, without labelling – data from literature); 19 – a – tentative boundary between pumpellyite occurrences in Tatric and "transitional" area, b – boundary at pumpellyite-free area of the Southern Veporic Unit (for further details see text).

(1985) was applied in this work. This division of the Central Western Carpathians (CWC for further) consists of the basic Alpine blocks – Tatric and Veporic units, which are confined by significant regional tectonic lines. These units built of the pre-Alpine basement rock-complexes enveloped with characteristic Late-Paleozoic – Mesozoic cover units (Andrusov et al., 1973; Maheľ, 1986 and cit. herein). The CWC is limited by the "Pieniny" Klippen Belt in the north and by the Lubeník-Margecany tectonic line limiting Veporic Unit from the south (Fig. 1). Tatric Unit was in Cretaceous ("pre-Gossau") time overthrusted with superficial nappes of Veporic affinity, depicted as Fatric nappe. Remarkable shear--zone of s. c. Pohorelá line divides the Northern and Southern Veporic Unit, which are mainly individualized by different Mesozoic cover sequences (Biely, 1964). Tectonically superposed Mesozoic nappes – Hronic and potentionally Silicic units are locally resting upon these units.

Basic tectonic development of CWC was completed in the Turonian time by the north-vergent shortening of all Western Carpathians units (Andrusov, 1968), which was parallelized with the closure of the South-Penninic (Ligurian) ocean (Tomek, 1993). Hronic Nappe-Unit represents a complicated large thrust sheet, tectonically placed over Tatric and Veporic units. Hronic volcano--sedimentary basin presumably originated in-between the Veporic and Gemeric Unit, before the Alpine collision (Andrusov, 1968; Biely and Fusán, 1967). Different model suggests common Hronic-Silicic nappe system, which was generated from the southernmost zones of the Inner Western Carpathians (Plašienka, 1999).

Temperature of Alpine metamorphism was estimated at 250–300 °C based on the illite crystallinity, composition of authigenic micas and deformation mechanisms in Tatric Mesozoic envelope sediments of the Malé Karpaty Mts. (Plašienka et al., 1993). A similar character of Alpine metamorphism, reaching anchizone or max. anchizone/greenschist metamorphic facies conditions, were also reported from Permian cover of Tríbeč core Mountains (Ďurovič et al., 1992) and Čierna hora Mts. of Northern Veporic Unit (Korikovskij et al., 1989; Lupták et al., 2003). Generalizing studies accorded with these data and there was also emphasized reaching greenschist facies metamorphism in Southern Veporic cover unit (Vrána, 1966b; Plašienka et al., 1989; Korikovskij et al., 1997a, b).

Basement rocks of the studied areas (Cambel, 1958; Maheľ, 1986; Putiš, 1992; etc.) are formed by variegated metamorphic complexes of Lower Paleozoic to potential Upper Proterozoic age. The basic metamorphic imprint was due to Hercynian regional metamorphism, usually confined between the middle greenschist – to upper amphibolite conditions. Metamorphic rock-units were frequently intruded and thermally reworked by Carboniferous granitoid intrusions. Metamorphosed volcano-sedimentary rocks of the westernmost situated *Malé Karpaty* (Little Carpathians) Mts. consist also of metasedimentary sequence, which was paleontologically proved as Devonian. Regional periplutonic manifestation of the Malé Karpaty granitoid massifs played significant role in metamorphic evolution of these rock-units. Basement of the *Považský Inovec Mts.* is divided according to lithological criteria and intensity of Alpine deformation into northern (Selec block) and southern (Bojná block) main parts. The northern block represents largely Alpine sheared metamorphic rock-complexes, whereas the southern block is rich in granitic masses and nearly completed Mesozoic nappe pile is preserved here. Amphibolitic bodies occur in relatively frequent amount in both blocks. The third studied core mountain range – *Západné Tatry* (Western Tatra) Mts. forms the western part of the Tatra Mts. halfhorst structure, which is truncated from Paleogene basin from the south. Basement rocks are composed of higher graded metamorphic rocks of siliciclastic and volcanic primary material and the Hercynian granitoid intrusion.

## Pumpellyite occurrences in CWC

First findings of pumpellyite in the Western Carpathians were reported from Permian effusive and subvolcanic basic rocks of the Hronic Unit (Vrána, 1966). Newly formed pumpellyite-prehnite-quartz mineral assemblage in Hronic Unit was connected with Alpine burial metamorphism (Vrána and Vozár, 1969). Low-temperature veins filled with pumpellyite and axinite were described from metamorphosed basic rocks of pre-Alpine basement in the Malé Karpaty Mts. (Vrána, 1966a). Pumpellyite was also noticed in garnet (rich in goldmanite-uvarovite component) – diopside-tremolite black schists of the same rock-unit (Uher et al., 2008). The secondary pumpellyite-prehnite--epidote mineral assemblage was introduced from Ca--skarn ("erlan") rock (Cambel et al., 1989). Low-graded alterations of plagioclase and biotite to pumpellyite were located in migmatite belt of the Tatric part of the Nízke Tatry Mts. (Spišiak and Pitoňák, 1993). Mineral assemblage with pumpellyite detected in tonalite alterations in the Malá Fatra Mts. formed during Alpine tectono-metamorphism (ca. 3 kb and 300 °C), whereas the older prehnite-bearing assemblage (<2 kb, 360–380 °C) was presumed as Hercynian (Faryad and Dianiška, 2003).

## Analytical methods

Chemical composition and identification of considered minerals were determined using the Cameca SX-100 electron microprobe in wavelength dispersive mode installed at the State Geological Institute of Dionýz Štúr in Bratislava (analysts I. Holický, V. Kollárová, P. Konečný, M. Kováčiková and P. Siman). Measurements of point analyses were carried out on polished thin sections covered by graphite. Operating conditions were set at 15 kV accelerating voltage and 20 nA beam current. For element analyses of silicate minerals following standards were used: Si (TAP, K$\alpha$, wollastonite), Al (TAP, K$\alpha$, $Al_2O_3$), Na (TAP, K$\alpha$, albite), K (LPET, K$\alpha$, orthoclase), Ca (LPET, K$\alpha$, wollastonite), Fe (LLIF, K$\alpha$, hematite), Mg (TAP, K$\alpha$, MgO), Mn (LLIF, K$\alpha$, rhodonite), Cr (LLIF, K$\alpha$, chromite), Ti (LPET, K$\alpha$, $TiO_2$). Standard electron beam size was set at 5 $\mu$m, in the case of minute phases it was focussed to 2 $\mu$m. The PAP routine was used.

**Location handlist of pumpellyite-bearing samples**

Following list is mostly linked to sample identification of analyses presented in Tabs. 1 and 2:

ZT 1+ biotite-amphibole gneiss, Western Tatra Mts., rock exposure, left bank side of Račkova valley at dam reservoir (alt. 900 m);

PI 2 grossular-epidote hornfels, Považský Inovec Mts. – Bojná part, debris at mountain ridge 2 km south from el. point Myslíkov vrch (790), west from recreation area Duchonka;

PI 3 garnetiferous amphibolite, Považský Inovec Mts. – Selec part, road-cut c. 800 m west from el. point Javorie (729), ca. 2.5 km NE from Selec village;

MK 4+ basic metatuffite rich in carbonaceous substance and pyrite-pyrrhotite mineralization, Malé Karpaty Mts., outcrop at old shaft in Rybníček area, ca. 8 km NWN of Pezinok;

MK 5 amphibolite (s.s.), Malé Karpaty Mts., forest road-cut 500 m NW from water reservoir, ca. 3 km NW from Pezinok;

MK 6+ diopside-amphibolite schist, Malé Karpaty Mts., forest outcrop in the vicinity of el. point 456, 700 m east from recreation area Slnečné údolie, north from Pezinok

## Petrology

Pumpellyite-bearing secondary mineral assemblages were identified in Pre-Alpine amphibolic crystalline schists, mostly in primary quartz-free lithology. Fine-grained pumpellyite mineral assemblage is usually associated with prehnite, zoisite, epidote, chlorite, albite, K-feldspar, calcite and quartz. Proportions of these minerals are in individual samples highly variable, many of them are frequently absent. Pumpellyite was preferentially formed due to replacement reaction from diopside and An-rich plagioclase, in less extend also from amphibole, garnet and biotite. In rare cases of sufficient size, pumpellyite is almost colourless or it shows greenish pleochroism and low birefringence colours with increasing of Fe-content.

Representative microprobe analyses of pumpellyite and prehnite are introduced in Tab. 1. Chlorite compositional geothermometry (Cathelineau, 1988) was applied for additional temperature and chemical appreciation of pumpellyite-(prehnite) assemblages (Fig. 2). However, chlorite was not found as the most typical constituent of the pumpellyite-prehnite alteration types in studied rocks. Despite the fact that the following lithological division is not always explicit, the pumpellyite occurrences in Tatric crystalline were tentatively divided into two principal rock-groups. They are further ranged according to the geographic name of concerned “core” mountains:

***– pumpellyite in calc-silicate rocks***

*The Považský Inovec Mts.* Along the northern zone of the *Bojná block* pumpellyite was found in small rock lens composed of plagioclase, epidote, grossularite-andradite garnet, diopside and amphibole. It developed along with chlorite by corrosion of albitized plagioclase, predominately. Chlorite and pumpellyite (Fig. 2A, analysis PI 2 in Tab. 1) are evidently the youngest phases, though their relation to epidote is not always clear. Composition of associated

Tab. 1
Representative microprobe analyses ($Fe^{2+}$ assumed as total Fe) of pumpellyite (+ in coexistence with analysed prehnite) and prehnite

| | pumpellyite | | | | | | | | | | | prehnite | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | PI 2 | MK 4+ | MK 4A | ZT 1+ | ZT 1A+ | ZT 1B+ | PI 3A | PI 3B | MK 5 | MK 6+ | | ZT 1+ | MK 6+ |
| $SiO_2$ | 37.86 | 36.76 | 36.97 | 37.87 | 37.42 | 37.35 | 37.11 | 36.13 | 37.94 | 37.86 | | 43.97 | 44.35 |
| $TiO_2$ | 0.03 | 0.00 | 0.00 | 0.01 | 0.00 | 0.04 | 0.00 | 0.08 | 0.01 | 0.02 | | 0.00 | 0.02 |
| $Al_2O_3$ | 25.85 | 25.77 | 26.85 | 25.41 | 26.22 | 23.69 | 26.30 | 20.69 | 27.20 | 26.29 | | 24.24 | 24.19 |
| $Cr_2O_3$ | 0.01 | 0.38 | 0.00 | 0.00 | 0.04 | 0.04 | 0.00 | 0.00 | 0.00 | 0.01 | | 0.00 | 0.00 |
| $FeO_{tot}$ | 5.42 | 2.11 | 0.00 | 2.88 | 4.63 | 4.81 | 1.86 | 10.33 | 2.32 | 3.63 | | 0.05 | 0.12 |
| MgO | 1.46 | 3.17 | 4.19 | 3.38 | 1.54 | 3.41 | 3.13 | 2.29 | 2.37 | 2.15 | | 0.00 | 0.02 |
| MnO | 0.15 | 1.86 | 1.29 | 0.05 | 0.02 | 0.02 | 0.14 | 0.10 | 0.16 | 0.21 | | 0.03 | 0.03 |
| CaO | 22.83 | 22.14 | 22.42 | 22.66 | 22.81 | 22.79 | 22.41 | 22.48 | 23.31 | 22.49 | | 26.60 | 25.92 |
| $Na_2O$ | 0.05 | 0.00 | 0.00 | 0.01 | 0.02 | 0.01 | 0.04 | 0.04 | 0.05 | 0.02 | | 0.07 | 0.23 |
| $K_2O$ | 0.00 | 0.08 | 0.08 | 0.04 | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | | 0.01 | 0.03 |
| Total | 93.66 | 92.27 | 91.80 | 92.31 | 92.72 | 92.15 | 90.99 | 92.13 | 93.37 | 92.68 | | 94.98 | 94.91 |
| | per 24.5 O | | | | | | | | | | | per 23 O | |
| Si | 6.070 | 5.952 | 5.927 | 6.085 | 6.028 | 6.088 | 6.017 | 6.096 | 6.012 | 6.072 | $Si^{IV}$ | 6.335 | 6.389 |
| Al | 4.885 | 4.918 | 5.073 | 4.812 | 4.979 | 4.551 | 5.026 | 4.114 | 5.080 | 4.970 | $Al^{IV}$ | 1.665 | 1.611 |
| Ti | 0.004 | 0.000 | 0.000 | 0.001 | 0.000 | 0.005 | 0.000 | 0.010 | 0.001 | 0.002 | $Al^{VI}$ | 2.451 | 2.496 |
| Cr | 0.000 | 0.049 | 0.000 | 0.000 | 0.005 | 0.005 | 0.000 | 0.000 | 0.000 | 0.001 | Ti | 0.000 | 0.002 |
| Mg | 0.349 | 0.765 | 1.001 | 0.810 | 0.369 | 0.829 | 0.757 | 0.576 | 0.560 | 0.514 | Cr | 0.000 | 0.000 |
| $Fe^{2+}$ | 0.727 | 0.286 | 0.000 | 0.387 | 0.624 | 0.655 | 0.252 | 1.458 | 0.307 | 0.487 | Mg | 0.000 | 0.004 |
| Mn | 0.020 | 0.255 | 0.175 | 0.007 | 0.003 | 0.003 | 0.019 | 0.014 | 0.021 | 0.029 | $Fe^{2+}$ | 0.006 | 0.014 |
| Ca | 3.922 | 3.841 | 3.851 | 3.901 | 3.936 | 3.980 | 3.893 | 4.064 | 3.958 | 3.864 | Mn | 0.004 | 0.004 |
| Na | 0.016 | 0.000 | 0.000 | 0.003 | 0.007 | 0.004 | 0.013 | 0.013 | 0.015 | 0.006 | Ca | 4.106 | 4.001 |
| K | 0.000 | 0.000 | 0.016 | 0.008 | 0.005 | 0.001 | 0.000 | 0.000 | 0.000 | 0.000 | Na | 0.018 | 0.064 |
| | | | | | | | | | | | K | 0.003 | 0.006 |
| M/MF | 0.324 | 0.728 | 1.000 | 0.677 | 0.372 | 0.559 | 0.750 | 0.283 | 0.646 | 0.513 | | | |
| pmp- | -(Al) | -(Al) | -(Mg,Al) | -(Al,Mg) | -(Al) | -(Mg) | -(Al) | -(Fe) | -(Al) | -(Al) | | | |

chlorite-(Fe) (see centre in Fig. 2A and analysis PI 2-1 in Tab. 2) indicates the formation temperature slightly over 200 °C (Cathelineau, 1988).

*The Malé Karpaty Mts.* The lithology of peculiar black schists, enriched in basic pyroclastic and carbonatic material, is closely related to calc-silicate rock-group. Alterations of these rocks are characterized also by prehnite and pumpellyite, which form relatively abundant component of groundmass alterations or grow at the expense of diopside (Fig. 2B, an. MK 4+ in Tab. 1). In the case of diopside and/or amphibole (“tremolite I”) replacement reactions, pumpellyite usually appears in the mixture with albite, new amphibole (“tremolite II”), chlorite and probably also phlogopite. Composition of coexisting chlorite (Tab. 2, an. MK 4-1) indicates here some 270 °C, though chlorite (an. MK 4-2) in pumpellyite-sericite submicroscopic aggregates from the groundmass yield temperature below 200 °C. Both these chlorites are exhibiting uncommonly high Ti and Mg content.

Occasionally, pumpellyite forms radial ca. 0.3 mm elongated nonpleochroic crystals of anomalous pure Mg--content (Tab. 1, an. MK 4A). Its occurrence is bound to micro-domains enriched in large pyrite crystals, which underwent local allochemical alteration resulting in forming of fine calcite, K-feldspar, quartz and pumpellyite. Unusual primary bulk-rock composition of this sample is also underlined by the high Mn-content in pumpellyites.

***– pumpellyite in amphibolic gneisses, amphibolites***

*The Západné Tatry Mts.* Pumpellyite and prehnite belong to abundant alteration products of plagioclase and amphibole. In amphibole replacement reactions pumpellyite appears in coexistence with chlorite (Tab. 2, an. ZT 1-1), epidote and presumably biotite (“biotite II”), which seems to be a little older in the succession of secondary minerals. Abundant fine-grained clinozoisite, zoisite, K-feldspar, muscovite, chlorite, prehnite and not frequent pumpellyite developed usually in zones of the plagioclase breakdown. Plagioclase (andesine) margin was largely affected by prehnitization (Tab. 1, ZT 1+), overgrown by chlorite (Tab. 2, ZT 1-2) in some places. Similarly, composition of chlorite (Tab. 2, ZT 1B-3) enclosing pumpellyite-(Mg) (Tab. 1, ZT 1B+) in another plagioclase alteration zone gives temperature over 300 °C, which is in accordance with other chlorite compositions in the Západné Tatry Mts.

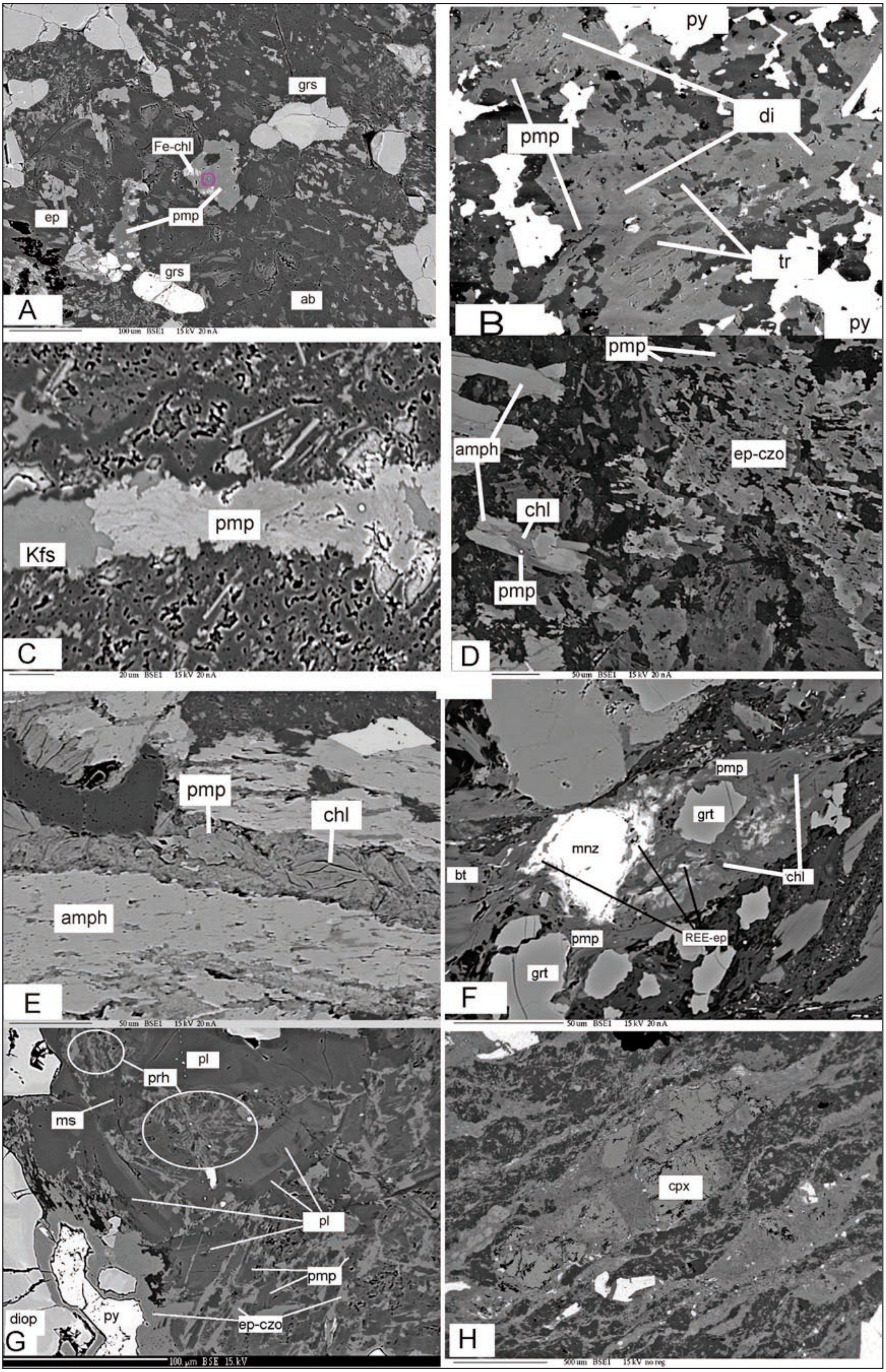
Irregularly distributed brittle micro-cracks are filled with pumpellyite – K-feldspar – calcite veinlets, representing relatively the youngest alteration episode of plagioclase. Thus, the tiny veinlet (Fig. 2C) is characterized by distinguishing chemical composition and both the pumpellyite analyses from the veinlet differ from each other by distinct M/MF ratio (see an. ZT 1+ and ZT 1A+ in Tab. 1; lighter and Fe-richer phase on the left hand side in Fig. 2C).

*The Považský Inovec Mts.* Petrographical study of amphibolite from the *Selec block* reminds, regardless of prehnite absence, alteration pattern described in the previous section. Primary metamorphic mineral assemblage composed of intermediary plagioclase, amphibole and garnet, was corroded by zonal epidote, zoisite, pumpellyite and chlorite (Fig. 2D). Chlorite (Tab. 2, PI 3B-2) grew simultaneously with pumpellyite (Tab. 1, PI 3A) at the expense of amphibole (Fig. 2D on the left) and indicated a relatively higher formation temperature, similar to these of the Západné Tatry Mts.

Alterations are also accompanied by tiny veinlets (Fig. 2E) filled with pumpellyite-chlorite-quartz assemblage. In -contrast to the above described wide-spread pumpellyite--(Al), this type is classified as pumpellyite-(Fe) (Tab. 1, PI 3B). Lower thermal conditions of this presumed declining alteration phase are also supported by low geothermometric estimation of concomitant chlorite (Tab. 2, PI 3B-1). Pumpellyite was also identified in the garnet–

Tab. 2
Microprobe analyses of chlorites coexisting with pumpellyite

| | PI 2-1 | MK 4-1 | MK 4-2 | ZT 1-1 | ZT 1-2 | ZT 1B-3 | PI 3B-1 | PI 3B-2 |
|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 29.29 | 31.86 | 33.78 | 27.39 | 26.96 | 27.59 | 29.83 | 26.37 |
| $TiO_2$ | 0.01 | 2.75 | 2.24 | 0.04 | 0.1 | 0.05 | 0.00 | 0.04 |
| $Al_2O_3$ | 21.40 | 18.96 | 17.58 | 20.14 | 20.59 | 20.32 | 16.38 | 19.45 |
| $FeO_{tot}$ | 30.08 | 4.36 | 7.74 | 21.48 | 22.14 | 21.82 | 23.85 | 26.21 |
| MgO | 4.85 | 30.05 | 25.22 | 17.81 | 17.34 | 17.33 | 17.08 | 14.16 |
| MnO | 0.35 | 0.00 | 0.25 | 0.37 | 0.4 | 0.35 | 0.37 | 0.46 |
| CaO | 0.33 | 0.00 | 0.19 | 0.14 | 0.12 | 0.14 | 0.18 | 0.16 |
| Total | 86.31 | 87.98 | 87.00 | 87.37 | 87.65 | 87.6 | 87.69 | 86.85 |
| per 28 O | | | | | | | | |
| $Si^{IV}$ | 6.320 | 5.955 | 6.457 | 5.658 | 5.560 | 5.680 | 6.197 | 5.630 |
| $Al^{IV}$ | 1.680 | 2.045 | 1.543 | 2.342 | 2.440 | 2.320 | 1.803 | 2.371 |
| $Al^{VI}$ | 3.646 | 2.131 | 2.417 | 2.562 | 2.567 | 2.611 | 2.209 | 2.520 |
| Ti | 0.002 | 0.387 | 0.322 | 0.006 | 0.016 | 0.007 | 0.000 | 0.007 |
| Mg | 1.528 | 8.373 | 7.186 | 5.486 | 5.330 | 5.320 | 5.290 | 4.506 |
| $Fe^{2+}$ | 5.314 | 0.681 | 1.237 | 3.712 | 3.819 | 3.760 | 4.143 | 4.678 |
| Mn | 0.062 | 0.000 | 0.040 | 0.064 | 0.070 | 0.061 | 0.065 | 0.083 |
| Ca | 0.076 | 0.000 | 0.039 | 0.030 | 0.027 | 0.031 | 0.041 | 0.037 |
| M/MF | 0.223 | 0.925 | 0.853 | 0.596 | 0.583 | 0.586 | 0.561 | 0.491 |
| T (°C) | 208 | 267 | 187 | 315 | 331 | 312 | 228 | 321 |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biotite gneiss (Fig. 2F) and amphibole diorite, occurring in the *Bojná block*. It is relatively widespread as in the *Selec block,* so in the *Bojná block*, but until now the prehnite has not been identified in the Považský Inovec Mts.

*The Malé Karpaty Mts.* Pumpellyite (Tab. 1, MK 5) replacing diopside was found in strongly altered amphibolitic body. Scarce diopside occurs only in close association with calcite, which has led to assumption of being formed from primary calcite-rich amygdule in basaltic rock during the periplutonic metamorphism (the local source-material of these minerals can be thought as related to the calc-silicate lithology).

Intense transformation with development of prehnite-pumpellyite-clinozoisite-epidote-muscovite assemblage was identified also in metamorphosed basic tuffs. Actinolite might be, due to its textural position, also associated with the above assemblage. Abundant pumpellyite and prehnite (Tab. 1, both an. MK 6+) occur in diopside, plagioclase and various types of primary amphibole. Prehnite originated predominately at the expense of basic plagioclase (Fig. 2G).

## Pumpellyite classification and geochemical background

According to pumpellyite classification (Passaglia and Gottardi, 1973), prevailing analyses fall in the field of pumpellyite-(Al) or to pumpellyite with nearly balanced content of Al and Mg (Tab. 1). Only exceptionally it corresponds with classification criteria (Mg or Fe content is higher than Al content in Y-structural position) for pumpellyite-(Mg) and pumpellyite-(Fe). Chemical composition of pumpellyite ZT 1B+ is noteworthy – it belongs to Mg-type, whereas the Fe-content is higher than Al-content in position Y. The only pumpellyite-(Fe) PI 3B is considered as $Fe^{2+}$ type (s. c. ferropumpellyite, Passaglia and Gottardi, 1973), coming out from the facts, that the Y-position does not contain any Fe and the sum of cations usually slightly oversteps the value 16.

Pumpellyite composition is, beside the primary lithologic predisposition, largely influenced by geochemistry of circulating fluids. This phenomenon can be documented by development of pumpellyite-(Al), regardless of it growths at the expense of diopside (Al-free environs) or basic plagioclase (andesine). Pumpellyite chemical classification is in great extent controlled by aluminium amount, whereas the M/MF ratio (or relative abundance of Mg and Fe) does not play a significant role. Similar phenomenon is valid for chlorites (Tab. 2) and accordingly for temperature estimation (Cathelineau, 1988), the most decisive is the Si and Al content and not the M/MF ratio.

On the other hand, pumpellyite more or less inherits certain components from its lithologic precursor. This can be demonstrated on uncommon sample (MK 4+, Tab. 1) with extreme enrichment of Mg and Mn. In accordance with function of protolith, chlorites of the same sample are anomalously rich in Ti content (Tab. 2). Prehnite crystallization shows stronger tendency to appropriate mineral precursor that represents mostly basic plagioclase in comparison to Mg-Fe alumo-silicate minerals.

## Temperature estimations

Composition of chlorite in coexistence with pumpellyite-bearing assemblages indicates temperatures between ca. 185 and 330 °C (see the last row in Tab. 2). Relatively higher temperatures of chlorites are caused by decreased Si vs. Al in tetragonal structural position as displayed in amphibole gneiss from the Západné Tatry Mts. (310 to 330 °C) and Považský Inovec Mts. (320 °C). On the other hand, the newly-formed chlorite from hydrothermal veinlets, or chlorite from calc-silicate rock in the Považský Inovec Mts., gives lower temperature values (ca. 220 ± 10 °C). Lower temperatures fits well with paragenetic pumpellyite-(Fe) located in tiny veinlets (Fig. 2E). In the Malé Karpaty area, two types of chlorites coexisting with pumpellyite were noticed in different textural and chemical micro-domains – the first one indicates ~270 °C and the second one ~190 °C.

An uniform evaluation of obtained data is not easy, because of small amount of analyses and various influences, which can be hardly quantified. Ambiguities comprise of the primary-rock material, host-mineral composition as well as the intensity and chemistry of external fluid input. Apart from some uncertainties, the metamorphic conditions of investigated mineral assemblages correspond in general with the pumpellyite-prehnite metamorphic facies. The low temperature part of this facies (around 200 °C) is indicated by the occurrence of pumpellyite-(Fe), lower temperatures obtained from chlorite thermometry and mineral fillings in brittle micro-cracks (in the Považský Inovec Mts.). On the contrary, if the chlorite records temperatures above 300 °C, pumpellyite is enriched in Mg and/or Al compound

◀**Fig. 2.** Scanning images of pumpellyite-bearing mineral assemblages (abbr.: pmp – pumpellyite, prh – prehnite, chl – chlorite, ab – albite, pl – plagioclase, Kfs – K-feldspar, amph – Ca-amphibole, tr – tremolite, ep – epidote, czo – clinozoisite, grs – grossular, grt – garnet, di – diopside, bt – biotite, ms – muscovite, py – pyrite) in crystalline rocks of Tatric crystalline basement (A-G) and Hronic gabbrodiorite (H). **A** – New-formed pumpellyite in size up to 0.1 mm gained sharp shapes; sample PI 2 grossular-epidote hornfels, Považský Inovec Mts.; **B** – Diopside (growing on expense of tremolite) is at edge replaced with pmp; MK 4+ basic metatuffite rich in carbonaceous substance; Malé Karpaty Mts.; **C** – Tiny veinlet penetrating through altered plagioclase; ZT 1+ biotite-amphibolite gneiss, Western Tatra Mts.; **D** – Intensive alteration of amphibole; increase in Fe marks light margin in epidotes on the right side, PI 3 garnetiferous amphibolite, Považský Inovec Mts.; **E** – Chlorite-pumpellyite veinlet crosscutting amphibole, loc. as to D; **F** – Abundant pumpellyite originated from biotite and garnet; around Hercynian monazite formed epidote rich in REE; garnet-biotite gneiss, Považský Inovec Mts.; **G** – Plagioclase replaced with prehnite (bordered by elipsoid), pumpellyite, epidote a muscovite; lighter, more basic plagioclase is corroded by acid plagioclase phases (central part of image); diopside-amphibole schist, MK 6+ Malé Karpaty; **H** – Clinopyroxene (in the middle) transformed to chlorite – actinolite ± epidote aggregate (light grey); plagioclase remnants (dark grey); ilmenite (shining); gabbrodiorite porphyry of Hronic Unit, loc.: ridge between elevation points 1 545 (Predná hoľa) and 1 263; 4 km W from Vernár village.

and newly-formed actinolite/tremolite, respectively biotite are noticed at places. These features represent the upper metamorphic limit of pumpellyite-prehnite facies, which borders with greenschist facies conditions.

## Tectono–metamorphic interpretations and discussion

The crystallization of prehnite and pumpellyite is clearly post-deformational process in relation to the primary mineral assemblage. By means of micro-textural criteria, other associated secondary minerals and their regional distribution, the Alpine (Cretaceous) metamorphism is suggested as the most reliable pumpellyite-forming process. Pumpellyite also post-dated the development of Alpine deformation structures and its origin was largely related to fluid reactivation during this collision tectonics. The imagined scheme of pumpellyite mineral assemblage distribution in the CWC area (Fig. 1) is outlined from aspect of the Alpine metamorphic evolution. Pumpellyite ± prehnite show rather symptomatic occurrence in Tatric Unit, mostly in its northern part (indicated by dotted-dashed line a). Based on recent knowledge, potential existence of pumpellyite or coexistence of pumpellyite with actinolite is supposed in uncertain "transitional" domain between the Tatric and Southern Veporic units. This domain may tentatively include southernmost Tatric areas (Tribeč Mts. and eastern part of the Nízke Tatry Mts.) and the Northern Veporic Unit. In the CWC the general south trending increase of Alpine reworking culminates in the Southern Veporic Unit (indicated by dotted-dashed line b in Fig. 1) which underwent to greenschist facies metamorphism, in general (Vrána, 1966b; Plašienka et al., 1989, and others). The Cretaceous processes overprinting amphibolitic basement-rocks are documented by development of new-formed actinolite, epidote, chlorite, Mg-rich biotite and albite (Kováčik et al., 1996), but no pumpellyite has been reported from the Southern Veporic Unit, so far. So, configuration of metamorphic degree within the CWC realm may also indirectly point to the Cretaceous age of pumpellyite-prehnite mineral assemblage.

The prehnite-pumpellyite-quartz mineral assemblage in Permian basic magmatic bodies of Hronic Unit was assigned to Alpine (Cretaceous) burial metamorphism (Vrána and Vozár, 1969). This facies typically occurs in Hronic tectonic overburden placed over Tatric and Northern Veporic units – up to the southernmost findings at Kvetnica spa near Poprad (c. f. Vrána, 1966; Vozár, 1976; Faryad and Jacko, 2002). It should be noted, that in recrystallized Permian basalts, placed in the vicinity of the "Pohorelá" line, southwards from Hranovnica village, there was described only new epidote, chlorite and actinolite (Vrána, 1966). Similar pumpellyite-free and chlorite-rich mineral assemblages (Fig. 2H) were found in the Hronic Upper Carboniferous and Permian basic rocks (Kováčik, 2008), which are resting upon the northern zone of the Southern Veporic Unit. These regional metamorphic crystallization features in Hronic Unit indicate much in common in respect to the pumpellyite distribution pattern in realm of CWC basement rocks. Pronounced deformation in localized shear zones of Upper Paleozoic sequence evidences that bottom parts of the Hronic Unit were also affected by the Alpine Intra-Veporic tectono-metamorphic processes. Pumpellyite-prehnite-quartz metamorphic facies development in Hronic Unit suggests a certain similarity to the alterations described in Tatric basement. Thus, all these data rather support conceptions about Hronic Unit as an integral part of CWC tectonic structure.

Indication of successive relation between the primary and the investigated low-temperature mineral assemblages appears in some of the studied samples. It mostly implies relatively higher thermal (>310 °C) pumpellyite ± prehnite ± actinolite ± biotite secondary paragenesis in amphibolitic basement-rocks. Remarkable overprinting structures were found in the pre-Alpine porphyric diopside, grossular and tremolite that were towards margin of crystals more-less gradually replaced by retrogressive pumpellyite ± prehnite bearing mineral assemblage. This kind of retrogressive reactions may be presumably placed to the latest Hercynian metamorphic phase that was connected with post-orogenic cooling and enhanced mobility of fluids.

Origin of pumpellyite entailed by Tertiary tectonic events can be theoretically admitted in the CWC, especially in the northern parts of Tatric Unit. Metamorphic response to collision dynamics related to closure of European foreland may represent one of the explainable solutions (Soták et al., 1999; Hrouda et al., 2002; Putiš, 2009). This accretion process might have hypothetically concerned pumpellyite--bearing and prehnite-free mineral assemblages located in the Považský Inovec Mts. Moreover, besides other reasons, a hydrothermal circulation during the Miocene uplift movements of the core mountains may play certain role, too. In the case of appropriate host-rock precursor, even more superimposed orogenetic events leading to pumpellyite formation cannot be excluded (e.g., pumpellyite of the Late Hercynian origin may not had been destructed during Alpine metamorphism, but a new generation could created).

## Conclusion

Secondary pumpellyite ± prehnite mineral assemblages were determined in metamorphic basement of the Malé Karpaty, Považský Inovec and Západné Tatry Mts. Their origin is closely related to pumpellyite-prehnite facies metamorphism, which is also supported by chlorite geothermometric estimations (~185 – 330 °C). Occurrence of pumpellyite-(Al) prevails, whereas pumpellyite-(Mg) or lower thermal pumpellyite-(Fe) developed only in places (Tab. 1). Pumpellyite was formed predomintaly in quartz-free lithology at the expense of pre-Alpine diopside, amphibole, biotite, garnet and fine-grained groundmass. Growth and composition of pumpellyite was widely influenced by the type and intensity of fluid infiltration. Prehnite replaced mainly An-rich plagioclase.

Relatively younger tiny veinlets are filled with the mineral assemblage pumpellyite – K-feldspar – calcite – chlorite and in many cases indicate conditions close to the lower parts of the prehnite-pumpellyite facies. Pumpellyites coexisting with the newly-formed biotite or tremolite/actinolite are approaching to the boundary of anchizone (subgreenschist) and greenschist facies metamorphism. Such specific mineral assemblages could have been formed during the late Hercynian cooling, eventually. In some cases (e.g. in the Považský Inovec Mts.), hypothetic Tertiary metamorphism driven by the closure of Penninic domains, cannot be safely ruled out. More proposed ways of pumpellyite formation are not in contradiction with each other.

Alpine (Cretaceous) tectono-metamorphism is thought to be the main forming process of studied mineral assemblages. Based on pumpellyite and/or actinolite occurrences, a tentative zonation of the Alpine metamorphism is outlined in the Central Western Carpathians (Fig. 1). This is in good accordance with the Alpine metamorphic reworking of the Hronic basic magmatic rocks. The absence of pumpellyite in the Southern Veporic basement coincides with actinolitic (pumpellyite-free) recrystallization mineral assemblages occurring in the southernmost locations of the Hronic basic rocks.

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