Metamorphic vanadian-chromian silicate mineralization in carbon-rich amphibole schists from the Malé Karpaty Mountains, Western Carpathians, Slovakia

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ABSTRACT

Mineralization, involving vanadian-chromian silicates, has been studied in Lower Paleozoic, carbon-rich amphibole schists with pyrite and pyrrhotite near Pezinok, southwest Slovakia. A detailed electron microprobe study has revealed the presence of V, Cr-rich garnet, clinozoisite, and muscovite, associated with amphiboles (magnesiohornblende, tremolite, actinolite, and edenite), diopside, and albite. The garnet contains 5–19 wt% V₂O₅, 5–11 wt% Cr₂O₃, and 2–13 wt% Al₂O₃ (16–64 mol% goldmanite, 19–36 mol% uvarovite, and 9–59 mol% grossular end-members). The garnet is unzoned or shows V-rich cores and Al-rich rims, or irregular coarse oscillatory zoning with V, Cr, and Al, locally involving Ca and Mn as well. The V, Cr-rich clinozoisite to mukhinite and “chromian clinozoisite” contains 2–9.5 wt% V₂O₅ and 1.5–11 wt% Cr₂O₃; the muscovite contains 2.5–8 wt% V₂O₅ and 0–7 wt% Cr₂O₃. The mineralization originated from primarily V-, Cr-, and C-rich mafic pyroclastic rocks, affected by volcano-exhalative processes. These rocks were weakly metamorphosed during early Hercynian regional metamorphism (M1), followed by late-Hercynian contact metamorphism (M2) with crystallization of V, Cr-rich silicates, diopside, amphiboles, phlogopite, titanite, albite, quartz, carbonate, pyrite, and pyrrhotite. The youngest Alpine (?) retrograde metamorphic event (M3) is connected with production of V,Cr-poor muscovite, clinochlore, clinozoisite, pumpellyite-(Mg), prehnite, quartz, and carbonates, under prehnite-pumpellyite facies conditions.

Keywords: V and Cr mineralization, amphibole schists, contact metamorphism, goldmanite, uvarovite, mukhinite, Western Carpathians, Slovakia

INTRODUCTION

Vanadium-rich silicate phases are found in mineral associations from metamorphosed fine-grained pyroclastic and clastic sediments rich in organic carbonaceous matter or from skarns, calcareous metapelites and marbles, associated with mafic rocks. Vanadian grossular to goldmanite [Ca₃(V₂(SiO₄))₃], a V-dominant member of the ugrandite garnet subgroup, is the most conspicuous mineral in such associations, together with other V-rich phases including micas, diopside, amphiboles, titanite, biotite, oxide minerals, and even sillimanite (e.g., Moench and Meyrowitz 1964; Karev 1974; Suwa et al. 1979; Benkerrou and Fonteilles 1989; Canet et al. 2003; Donohue and Essene 2005). Moreover, goldmanite has been described in refractory inclusions from the Leoville carbonaceous chondrite (Simon and Grossman 1992). Vanadian clinozoisite to mukhinite [Ca₃Al₂V₃⁺(Si₂O₇)(SiO₄)O(OH)], in association with goldmanite, has been described in marbles from the Tashegilskoye deposit, Siberia, Russia (Shepel and Karpenko 1969). Vanadian epidote to allanite occurs in association with goldmanite, vanadoan muscovite, vanadoan titanite, and tomichite in the main ore zone of the Hemlo gold deposit, Ontario, Canada (Pan and Fleet 1991, 1992).

The above-mentioned minerals are V-rich but relatively Cr-poor in most localities. However, in the Poblet area, Spain, V- and Cr-rich goldmanite and other minerals have been described (Canet et al. 2003). Donohue and Essene (2005) have also described chromian hercynite with vanadoan sillimanite. Our investigated occurrences in the Pezinok-Pernek crystalline complex, Malé Karpaty Mountains, Slovakia, represent another example of a rare V- and Cr-rich metamorphic association containing garnet (goldmanite-uvarovite-grossular s.s.) with other V- and Cr-rich silicate minerals. Preliminary results were reported by Uher et al. (1994). New mineralogical and petrogenetic results, based on detailed electron-microprobe analysis (EMPA) and X-ray diffraction (XRD) data, are the subject of this contribution.

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**Regional Geology**

The Pezinok-Pernek crystalline complex (PPCC) is a part of the pre-Alpine basement of the Central Western Carpathians. The PPCC represents volcano-sedimentary sequences of Lower Paleozoic metamorphic rocks, mainly metapelites to metapsammites, metabasaltic rocks, black schists, rarely quartzites, all of which have been intruded by Hercynian orogenic granitic plutons (Cambel 1958; Buday et al. 1962; Cambel and Khun 1983), ca. 20 km NE of Bratislava in SW Slovakia (Fig. 1). The PPCC is situated in the Malé Karpaty Mountains, the westernmost situated horst structure of the Ttric Superunit, a link between the Western Carpathians and the Eastern Alps (Maheľ 1986).

Palynological study indicates a Silurian to Devonian age for the PPCC volcano-sedimentary sequences (Cambel and Planèrová 1985). The geological structure of the PPCC was formed during the Hercynian (Devonian to Carboniferous) orogeny and collisional exhumation of oceanic crust represented by the Pernek Group on the metamorphosed, passive continental margin of the pre-Alpine basement of the Central Western Carpathians. The PPCC volcano-sedimentary sequences of Lower Paleozoic metamorphic rocks, mainly metapelites to metapsammites, metabasaltic rocks, black schists, rarely quartzites, all of which have been intruded by Hercynian orogenic granitic plutons (Cambel 1958; Buday et al. 1962; Cambel and Khun 1983), ca. 20 km NE of Bratislava in SW Slovakia (Fig. 1). The PPCC is situated in the Malé Karpaty Mountains, the westernmost situated horst structure of the Ttric Superunit, a link between the Western Carpathians and the Eastern Alps (Maheľ 1986).

**Analytical Methods**

The chemical compositions of the V-Cr silicate minerals were determined using a JEOL JXA 733 Superprobe and a Cameca SX100 electron microprobe in wavelength dispersive mode at the Geological Survey of the Slovak Republic, Bratislava. Operating conditions were set at 15 kV accelerating potential, 20 nA beam current and 3–5 µm beam diameter for analyses of garnet, amphiboles, and diopsides, and 15 kV, 10 nA and 10–15 µm for analyses of micas, chlorite, pumpellyite, prehnite, and feldspar. The following standards were used: synthetic SiO$_2$ (SiKo), TiO$_2$ (TiKo), Al$_2$O$_3$ (AlKo), metallic V (VKo), chromite (CrKo), hematite (FeKo), rhodonite (MnKo), MgO (MgKo), wollastonite (CaKo), barite (BaKo), albite (NaKo), and orthoclase (KAlO$_2$). The EMP detection limit for the measured elements was 0.05 to 0.1 wt%. The measurement accuracy varied between ±0.1 to 0.5 wt% under optimal operating conditions. For data processing, the overlap correction and PAP routine of Pouchou and Pichoir (1985) was used.

Data were collected on garnet with a Philips PW 1710 X-ray diffractometer at the Geological Institute, Slovak Academy of Sciences, Bratislava. CuKo was used, with instrumented conditions of 35 kV voltage, 20 nA current, and a 0.3° 2θ/min goniometer speed. Lattice parameters were calculated using the unit-cell software of Holland and Redfern (1997).

The crystal structure of a birefringent garnet was studied by single-crystal X-ray diffraction. The sample was shaped to an ellipsoid with the main radii of 0.125, 0.125, and 0.15 mm using a compression air grinder. Room-temperature diffraction data (28.26 reflections with $-13 \leq h \leq 13, -15 \leq k \leq 14, -14 \leq l \leq 14, 26_{max} = 53.43^\circ$) were collected on a Bruker AXS Kappa X8 APEX II X-ray automodule diffractometer (MoKα radiation, graphite monochromator) equipped with a CCD detector.

**Results**

**Petrography and rock composition**

The host rocks are fine- to medium-grained, dark-gray schists (commonly named black schists) with varying amounts...
of primary clastic and tuffaceous mafic components. The rocks have a fine-grained groundmass with larger porphyroblastic aggregates of amphibole, garnet, pyroxene, plagioclase, pyrite, and several other minerals. Due to a systematic black carbon admixture, they could be referred to as C-rich amphibole schists with pyrite ± pyrrhotite.

The groundmass is very fine grained with visible metamorphic foliation and lepidogranoblastic to nematiclastic texture (see Fig. 5c, later in this paper). Due to the small size of the crystals (mainly 20 to 100 μm), as well as the common presence of opaque black carbon particles, the minerals of the groundmass were difficult to distinguish under the optical microscope. Therefore, they were studied using back-scattered electron (BSE) imaging and EMPA. The groundmass (see Fig. 5c, later in this paper) consists of albite (+plagioclase), quartz, amphibole, phlogopite, chlorite, muscovite, pumpellyite, titanite, and pyrite. Carbonaceous matter mainly has an organic origin and has been metamorphosed to the metaanorthacite-semigraphite stage with low contents of bitumen (Cambel et al. 1985; Molák and Slavkay 1996). The C-rich amphibole schists show a large compositional variability, mainly in Fe, Mg, Na, and K, but generally they are Al-depleted and enriched in V, Mn, Ni, Co, and Cu (Table 1).

Mineral description

The garnet belongs to goldmanite-grossular-avarrovarite solid-solution series, with the goldmanite end-member predominating (Uher et al. 1994). The green garnet was originally called “uvarovite” when it was discovered in the Rybníček deposit near Pezinok (Cíllík et al. 1959). It takes the form of dark emerald-green, semi-transparent crystals with {110} and more rarely {221} crystal faces. Fresh surfaces have a slight glassy luster, whereas weathered crystals and aggregates are pale green (Fig. 2a). The size of the crystals is typically 1–2 mm, rarely up to 5 mm; aggregates can reach up to 2 cm in size. Under the microscope, it is pale green with a distinct anomalous birefringence characterized by irregular optical domains (Fig. 2b). The garnet is associated with amphibole, pyrite, pyrrhotite, albite (Figs. 2c–2d), and commonly contains inclusions of pyrite/pyrrhotite and carbonaceous matter. Locally, garnet crystals show a skeletal atoll-like shape in association with tremolite (amphibole I) and albite (Fig. 2d).

EMPA reveals strong variations in V, Cr, and Al, i.e., within goldmanite-avarrovarite-grossular solid solutions (Fig. 3). These analyses show 5–19 wt% V2O3, 5–11 wt% Cr2O3, and 2–13 wt% Al2O3, corresponding to 16–64 mol% goldmanite, 19–36 mol% of uvarovite, and 9–59 mol% of grossular (Table 2; Fig. 3). The largest compositional variations are between V and Al. The V/Cr atomic ratio varies only slightly (ca. 2.5–3). The V, Cr, and Al contents of garnet are characteristic for each of the studied localities. For example, garnet from Lower Augustín a Michal adits has the highest V contents (up to 22 wt% V2O3 or 73 mol% goldmanite), whereas garnet from the Rybníček and especially Lower Augustín adits have the highest Al contents (up to 13 wt% Al2O3 or 59 mol% grossular) and the lowest V contents (5 wt% V2O3 or 16 mol% goldmanite). Uvarovite-dominant compositions with 10 wt% Cr2O3, 9.5 wt% V2O3, and 7.5 wt% Al2O3 (34 mol% uvarovite, 32 mol% goldmanite, and 33 mol% grossular end-member) were formerly described only in Rybníček (Uher et al. 1994). The garnet is unzoned or shows V-rich cores and Al-rich rims or irregular coarse oscillatory zoning with variations in V, Cr, and Al (Fig. 4). Irregular variations in Ca and Mn are also present (Table 2).

The measured cell dimension of the garnet is in the range of 12.001(1)–12.043(1) Å, which is consistent with published data for goldmanite (Moench and Meyrowitz 1964; Strens 1965; Filippovskaya et al. 1972; Litocheł et al. 1985; Benkerrou and Fonteilles 1989; Hallsworth et al. 1992) as well as with our older data for goldmanite from Rybníček [11.969(1)–12.000(6) Å; Uher et al. 1994].

To evaluate the origin of anomalous birefringence, the crystal structure of one sample was studied using the single-crystal XRD method. Although the measured unit-cell dimensions [a = 12.003(4) Å, b = 11.991(5) Å, c = 12.009(5) Å, α = 90.12(3)°, β = 90.04(3)°, γ = 90.04(3)°] were close (within 4σ) to the ideal cubic one, the presence of anomalous birefringence, differences in the intensities of equivalent reflections, and the appearance of forbidden reflections pointed to a triclinic symmetry typical for natural Ca garnets (Wildner and Andrut 2001; Shtukenberg et al. 2005 and references therein). Refined of the crystal structure was performed using the SHELXL program package (Sheldrick 1997) for the ideal cubic space group $Ia\overline{3}d$ [$R = 0.0244$ for 149 unique reflections with $F_o > 4\sigma(F_o)$, $R_m = 0.0633$] as well as in the triclinic space group $I$ [$R = 0.0534$ for 2533 unique reflections with $F_o > 4\sigma(F_o)$, $R_m = 0.1744$]. The high $R$-value obtained for the triclinic space group did not allow for it to be preferred it to the cubic one. As a consequence, the final atomic coordinates are presented for the cubic variant only (Tables 3 and 4).

The data agree with the general formula $\text{Ca}_9\text{M}_2(\text{SiO}_4)_8$, where the M site is occupied by Al, V, and Cr. Unfortunately, XRD is unable to distinguish which of the three different cations occupies the M site without constraints on the crystal composition.

### Table 1. Representative chemical analyses of C-rich amphibole schists from the PPCC

<table>
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<tr>
<th>Sample no.</th>
<th>Locality</th>
<th>Locality</th>
<th>Locality</th>
<th>Locality</th>
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<tr>
<td></td>
<td>Pezinok, Rybníček adit</td>
<td>Pezinok, Michal adit</td>
<td>Pezinok, Cajla mine</td>
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<td>SiO$_2$</td>
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<td>54.64</td>
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<td>Al$_2$O$_3$</td>
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<td>5.68</td>
<td>6.54</td>
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<tr>
<td>FeO$_{total}$</td>
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<td>18.32</td>
<td>10.59</td>
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<td>0.05</td>
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<td>C$_{org}$</td>
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<td>n.a.</td>
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<td>L.O.I.</td>
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<td>13.88</td>
<td>6.15</td>
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<tr>
<td>Total</td>
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<td>100.01</td>
<td>98.45</td>
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<tr>
<td>V</td>
<td>11.50</td>
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<td>720</td>
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<tr>
<td>Cr</td>
<td>760</td>
<td>224</td>
<td>60</td>
<td></td>
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<tr>
<td>Ni</td>
<td>60</td>
<td>1080</td>
<td>288</td>
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<tr>
<td>Co</td>
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<td>19</td>
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<tr>
<td>Cu</td>
<td>229</td>
<td>300</td>
<td>209</td>
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<tr>
<td>U</td>
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<tr>
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<tr>
<td>Ba</td>
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<td>1910</td>
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</tr>
</tbody>
</table>

Notes: Main elements and organic carbon (C$_{org}$) in wt%, trace elements in ppm; Ry-1 and MI-1 (this work), 62 A (Cambel and Khun 1983). The compositions determined by XRF (main elements), conductometry (C$_{org}$) and optical spectroscopy (OES); analytical conditions as Cambel and Khun (1983).
Table 2. Representative compositions of silicate minerals from C-rich amphibole schists of the PPCC (wt%)

| Locality   | Sample | Rybníček | Rybníček | Augustin | Rybníček | Augustin | Rybníček | Augustin | Rybníček | Augustin | Rybníček | Rybníček | Rybníček |
|------------|--------|-----------|-----------|----------|-----------|----------|-----------|----------|-----------|----------|-----------|-----------|-----------|----------|
|            |        | RY127     | RY124     | DA1112   | RY135     | DA118    | RY13      | DA113    | RY626     | DA4a     | RY423     | DA4a     | RY14a     | RY110    |
| SiO₂       | 35.85  | 37.17     | 36.63     | 37.46    | 37.29     | 50.98    | 56.58     | 48.07    | 54.67     | 54.38    | 54.13     |           |           |          |
| TiO₂       | 0.00   | 0.00      | 0.32      | 0.03     | 0.22      | 0.00     | 0.00      | 0.99     | 0.00      | 0.00     | 0.00      |           |           |          |
| Al₂O₃      | 2.02   | 6.76      | 4.09      | 8.69     | 6.69      | 10.68    | 7.59      | 2.56     | 11.64     | 2.86     | 2.31      | 1.39      |           |          |
| V₂O₅       | 18.93  | 14.59     | 16.15     | 10.19    | 6.98      | 6.10     | 2.58      | 0.65     | 0.00      | 0.40     | 1.01      |           |           |          |
| Cr₂O₃      | 8.36   | 6.15      | 8.24      | 8.20     | 11.39     | 9.01     | 0.64      | 0.00     | 0.00      | 0.00     | 0.42      |           |           |          |
| FeO        | 0.13   | 0.20      | 0.00      | 0.34     | 0.51      | 0.56     | 0.25      | 0.26     | 0.20      | 5.10     | 2.37      | 0.00      |           |          |
| MnO        | 0.75   | 1.42      | 1.37      | 2.36     | 4.32      | 0.00     | 0.00      | 1.83     | 0.00      | 0.00     | 0.00      |           |           |          |
| MgO        | 0.00   | 0.09      | 0.00      | 0.04     | 0.02      | 0.29     | 21.12     | 23.46    | 21.22     | 18.96    | 16.50     | 17.17     |           |          |
| CaO        | 33.42  | 33.59     | 33.51     | 32.88    | 32.15     | 31.09    | 12.81     | 13.50    | 13.44     | 12.54    | 23.47     | 24.57     | 100.03    | 99.67    |
| Na₂O       |        |           |           | 1.40     | 0.35      | 2.20     | 0.63      | 0.52     | 0.98      |           |           |           |           |          |
| K₂O        |        |           |           | 0.00     | 0.15      | 0.18     | 0.00      | 0.08     | 0.00      |           |           |           |           |          |
| H₂O        |        |           |           | 2.16     | 2.20      | 2.17     | 2.12      |           |           |           |           |           |           |          |
| Total (calculated) | 99.46 | 99.97 | 100.31 | 100.19 | 100.14 | 100.28 | 99.53 | 99.71 | 100.11 | 98.71 | 100.03 | 99.67 |
| Number of O atoms | 12 | 12 | 12 | 12 | 12 | 12 | 23 | 23 | 23 | 23 | 6 | 6 |

Figure 2. Garnet (goldmanite-grossular-ufarovite s.s.) from C-rich amphibole schists. (a) Crystal morphology. (b) Birefringence of garnet (Gld) in amphibole-quartz-pyrite/pyrrhotite-bearing metabasic pyroclastic rock (crossed polars). (c) Garnet (Gld) in association with pyrite/pyrrhotite (Py, white areas) and silicate minerals (dark gray to black), BSE image. (d) Atoll-shaped garnet (white areas) with amphibole I (Amp I) and albite (Ab), BSE image. (a-c) Rybníček adit, (d) Lower Augustín adit. Scale bars on each image represent 500 µm.
Therefore, initially the M site was assumed to be occupied by Al and V. Crystal structure refinement gave the composition of the M site as \( \text{Al}^{0.27(1)}\text{V}^{0.73(1)} \) (i.e., \( \sim 20.3 \) electrons per site). Since V and Cr have nearly the same atomic scattering factors, the amount of Al should be close to the true value. EMPA data show that the atomic V/Cr ratio is nearly constant (see above) and equal to approximately 2, for a sample composition of \( \text{Ca}_3(\text{Al}^{0.29(1)}\text{V}^{0.47(1)}\text{Cr}^{0.24(1)})_2(\text{SiO}_4)_3 \). The crystal structure is very close to that of goldmanite \( \text{Ca}_3(\text{Al}^{0.24}\text{V}^{0.6}\text{Fe}^{0.16})_2(\text{SiO}_4)_3 \) (Novak et al. 1994).
Cr$_2$O$_3$ (0.1 Cr apfu) occur in amphibole I; Al$_2$O$_3$ contents range up to 2.6 wt% V + Fe) = 0.95–1 (Table 2; Fig. 6a). Commonly, elevated V and Cr is classified as tremolite to magnesiohornblende (Leake et al. 1997) with nearly pure Mg end-members composition: [Mg/(Mg + Fe) = 0.95–1 (Table 2; Fig. 6a)]. Rarely, amphibole I$_{ed}$ (edentine-rich amphibole) occurs rarely in association with amphibole I porphyroblasts, forming smaller euhedral to subhedral crystals up to 0.5 mm in size. Amphibole I$_{ed}$ could be classified as edentine according to the nomenclature of Leake et al. (1997) despite the relatively low Na content [1.7–2.2 wt% Na$_2$O, 0.45–0.59 Na apfu, 4[Na+K] = 0.50–0.62 apfu] compared to the edente end-member. The edente has a very high Mg/Fe ratio [Mg/(Mg + Fe) = 0.99–1], a lower Si content (48.1 – 48.5 wt% SiO$_2$, 6.63–6.74 Si apfu), and a higher total Al content (9.7–11.6 wt% Al$_2$O$_3$, 1.59–1.89 Al apfu) in comparison to the other studied amphiboles (Table 2; Fig. 6b). The studied edente is V-poor, but it contains up to 1.5 wt% Cr$_2$O$_3$.

Amphibole II forms rare small subhedral to anhedral crystals (up to 0.1 mm in size) that locally replace amphibole I and diopside and is in close association with a younger generation of albite. Amphibole II compositions lie near the actinolite-tremolite boundary with Mg/(Mg + Fe) = 0.84 – 0.92 (Fig. 6a). Aluminum contents (0.8–2.9 wt% Al$_2$O$_3$) are lower in comparison to amphibole I. Neither V nor Cr were detected (Table 2). Generally, the distribution of V and Cr in all the amphiboles is irregular without any systematic distribution within the crystal. The V$^{3+}$ and Cr$^{3+}$ cations are located on the C-position in the amphibole together with Al$^{3+}$ as part of the coupled substitution $^4$(Mg,Fe$^{3+}$)$_2$Si$^4$(Al,V,Cr)$_2$Al$_1$.

Diopside is less common but characteristic of the peak metamorphic stage for these rocks. It forms anhedral to subhedral grains, rarely euhedral columnar crystals, up to 0.5 mm in length. In many cases, diopside overgrows amphibole I, but locally diopside relics in amphibole were also identified (Fig. 5b). Locally, diopside appears in spatial relation with albite. Quartz-calcite veinlets with diopside also occur. This phenomenon indicates a partly metasomatic origin for the diopside, connected with a fluid influx, probably associated with the Modra tonalite-granodiorite contact aureole. EPMA indicates a nearly pure diopside composition, with up to 2.5 wt% Al$_2$O$_3$, 1.7 wt% V$_2$O$_5$, 0.4 wt% Cr$_2$O$_3$, and 2.5 wt% FeO (Table 2).

Plagioclase is a characteristic phase of the groundmass (Fig. 5c); locally both nearly pure albite and a rare intermediate plagioclase (An$_{0.9-1}$) occur together. The coexistence of both plagioclase compositions seems to be the result of disequilibrium conditions during a relatively short-term contact-thermal metamorphic event. Moreover, near end-member albite (An$_{0.98}$-An$_{1.0}$) forms anhedral to subhedral crystals, 0.1 – 0.3 mm in size, in association with garnet, diopside, clinzoisite I, and amphibole (Figs. 2d, 5a, 5d, and 5e). Some of the albite may have formed during more recent retrograde metamorphism.

Clinzoisite forms anhedral porphyroblasts (up to 0.5 mm in size) or fine-grained aggregates. Porphyroblasts (clinzoisite I) are commonly zoned and show a greenish pleochroism. This clinzoisite is syngenetic to slightly younger diopside. Microscopic observations indicate that clinzoisite I and amphibole I (tremolite) are not found together. Clinzoisite I, in many cases, crystallized with diopside, but tremolite is always associated with diopside, not with clinzoisite I (Figs. 5a and 5d). Clinzoisite I contains 2.1–9.5 wt% V$_2$O$_5$ and 1.4–11.3 wt% Cr$_2$O$_3$.

### Table 3

Fractional atomic coordinates and isotropic displacement parameters $U_{iso}$ of the garnet crystal structure refined in the space group $Ia3d$ (Rybníček adit)

<table>
<thead>
<tr>
<th>Site</th>
<th>$x/a$</th>
<th>$y/b$</th>
<th>$z/c$</th>
<th>$U_{iso}$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0068(5)</td>
</tr>
<tr>
<td>Ca</td>
<td>0</td>
<td>0.25</td>
<td>0.125</td>
<td>0.0094(4)</td>
</tr>
<tr>
<td>Si</td>
<td>0</td>
<td>0.25</td>
<td>0.375</td>
<td>0.0086(5)</td>
</tr>
<tr>
<td>O</td>
<td>0.03912(14)</td>
<td>0.04763(13)</td>
<td>0.65442(13)</td>
<td>0.0100(6)</td>
</tr>
</tbody>
</table>

### Table 4

Anisotropic displacement parameters, $U_{ij}$ (Å$^2$) of the garnet crystal structure refined in the space group $Ia3d$ (Rybníček adit)

<table>
<thead>
<tr>
<th>Site</th>
<th>$U_{11}$</th>
<th>$U_{22}$</th>
<th>$U_{33}$</th>
<th>$U_{12}$</th>
<th>$U_{13}$</th>
<th>$U_{23}$</th>
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</thead>
<tbody>
<tr>
<td>M</td>
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<td></td>
<td></td>
<td>0.0003(2)</td>
<td>0.0003(3)</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
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<td>0</td>
<td>0</td>
<td>0.0013(3)</td>
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<tr>
<td>Si</td>
<td>0.0092(6)</td>
<td>0.0075(7)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>0.0122(10)</td>
<td>0.0090(10)</td>
<td>0.0089(9)</td>
<td>0.0007(7)</td>
<td>-0.0002(7)</td>
<td>0.0003(6)</td>
</tr>
</tbody>
</table>
Some compositions reach mukhinite and “chromian clinozoisite” compositions (Table 2; Fig. 7). The compositions with V > (Al,Cr) in the M3 position belong to mukhinite, whereas one Cr-rich composition (0.713 Cr apfu, Table 2) indicates the presence of a Cr-dominant member in the M3 position (Fig. 7). However, preliminary structural results for Cr-rich clinozoisite or epidote (called “tawmawite”), from Outokumpu, Finland, indicate that Cr is disordered over the M3 and M1 positions. This finding casts doubt on the validity of the Cr-dominant member if Cr < 1 apfu.

The name chromian (or Cr3+-rich) clinozoisite is preferred until new evidence is presented (Armbruster et al. 2006). Fine-grained clinozoisite II, without V and Cr, is the product of retrograde low-temperature metamorphism together with V,Cr-free clinochlore, pumpellyite-(Mg), muscovite II, and possibly albite II.

Muscovite forms subhedral, lamellar, greenish crystals, up to 1 mm in size, in association with amphibole I, quartz I, and pyrite/pyrrhotite (Fig. 5f) or tiny, up to 0.1 mm, subhedral to anhedral, colorless crystals in the groundmass, which reflects the original clay content of the source rocks. Two muscovite generations are recognized: V,Cr-rich muscovite I with 2.5–8 wt% V₂O₅ and 0–7 wt% Cr₂O₃ (0.12–0.45 apfu V and Cr, respectively) and V,Cr-free muscovite II with ≤0.4 wt% V₂O₅ and Cr₂O₃ (Table 2; Fig. 8). VAl₁ and CrAl₁ are the most evident substitution mechanisms in muscovite I (Fig. 8). Locally, Ba-rich muscovite II was detected (Table 2). Vanadium,(Cr)-rich
Anhedral quartz grains and aggregates are found in the groundmass of amphibole I, edenite (open circles). The PPCC. (a) Amphibole I (gray circles), amphibole II (black triangles). (b) Amphibole I, edenite (open circles).

Muscovite I formed during high-grade contact metamorphism together with garnet, amphibole, diopside, and V, Cr-rich clinozoisite I, whereas V, Cr-free muscovite II is related to younger, retrograde processes.

Phlogopite of nearly pure Mg composition \( \text{Mg} / (\text{Mg} + \text{Fe}) = 0.97–0.98 \) (Table 2), is closely associated with clinochlore in some samples (Fig. 5c). In rare cases, phlogopite forms fan-like aggregates up to 0.5 mm in size. The crystallization of phlogopite is probably connected with the formation of diopside, garnet, and both amphibole generations.

Chlorite is non-pleochroic with gray interference colors, and corresponds to the Mg end-member clinochlore with Mg/(Mg + Fe) = 0.93–0.98 (Table 2). Clinochlore is syngentic to slightly younger phlogopite. Crystallization of chlorite, like albite, was probably the product of manifold metamorphic events; both during contact metamorphism as well as during secondary alteration.

Titanite forms small euhedral to subhedral crystals in the groundmass (Fig. 5c) as well as in association with diopside, albite, clinozoisite I, and pyrite/pyrrhotite. Fluorapatite forms as rare, anhedral, 20–35 \( \mu \)m grains in association with amphibole I and diopside pyrophylloslasts.

Pumpellyite occurs as a typical alteration product of the groundmass and pyrophylloslasts. Locally zoned pumpellyite, in association with albite, replaces diopside and amphibole I (Fig. 5e). It forms scarce fine, fan-shaped aggregates. EMPA reveal pumpellyite-(Mg) compositions \( \text{Mg} / (\text{Mg} + \text{Fe}) = 0.70–0.99 \), to be relatively enriched in Al (Table 2). Prehnite is a rare phase and forms subhedral grains (up to 0.1 mm) in association with clinozoisite II. It shows a nearly pure end-member composition (Table 2). Anhedral quartz grains and aggregates are found in the groundmass of amphibole II, edenite (open circles).

**FIGURE 6.** Amphibole compositions from C-rich amphibole schists of the PPCC. (a) Amphibole I (gray circles), amphibole II (black triangles). (b) Amphibole I, edenite (open circles).

**FIGURE 7.** Ternary V-Al-Cr diagram of epidote group minerals from C-rich amphibole schists of the PPCC.

or form late hydrothermal veinlets and quartz-rich zones.

Calcite forms interstitial grains scattered in the groundmass (up to 0.3 mm large) or irregular veinlets and domains with quartz. Primary carbonates were not detected in the groundmass. The presence of calcite and siderite in these rocks is probably related to the influence of younger, granite-related, post-magmatic, mainly hydrothermal fluids. However, the pre-metamorphic existence of minor calcite can be indirectly assumed to be due to the later crystallization of Ca-bearing metamorphic silicates. Local, late hydrothermal siderite forms fine-grained aggregates or coarse-grained veinlets (up to 3 mm thick) associated with quartz.

Pyrite is widespread. It forms euhedral to subhedral hexahedric crystals in the groundmass and 0.01–5 mm crystals in association with amphiboles, diopside, garnet, and pyrrhotite. In some cases, subhedral pyrite forms 0.1–0.2 mm large inclusions in goldmanite. Small pyrite crystals and fine-grained aggregates are an inseparable part of the primary rock composition and locally form a stratiform pyrite mineralization. However, the larger pyrite crystals are likely to have formed with other porphyroblastic phases in the course of later metamorphic events.

Irregular, fine-grained pyrrhotite aggregates (usually up to 5 cm in size) are common locally. Pyrrhotite is associated with amphiboles, garnet, quartz, and pyrite. Crystallization and/or recrystallization of the Fe sulfide stratiform mineralization may have occurred over a wide time span ranging from diagenesis to metamorphism and remobilization during late hydrothermal alteration. Rare chalcopyrite forms anhedral grains (up to 15 \( \mu \)m in size) in association with late siderite and quartz veinlets. Rare, subhedral to anhedral uraninite grains, 5–25 \( \mu \)m in size, were detected at the contact of pyrrhotite and unspecified silicate minerals in the Rybníček adit (Cambel et al. 1977).

**PETROGENETIC EVOLUTION OF V-CR MINERALIZATION: INTERPRETATION AND DISCUSSION**

Vanadium-rich silicate mineralizations have been described in a series of localities. These consist of goldmanite (or V-rich garnet) and/or V-rich micas, amphiboles, pyroxenes, clinozoisite,
titane, spinels, and other minerals (e.g., Moench and Meyrowitz 1964; Momoi 1964; Shepel and Karpenko 1970; Filippovskaya et al. 1972; Karev 1974; Suwa et al. 1979; Benkerrou and Fonteilles 1989; Pan and Fleet 1992; Jeong and Kim 1999). However, in each of these cases, the Cr content in the minerals and rocks was usually low. On the other hand, metamorphic Cr-rich assemblages with uvarovite and other Cr-bearing silicates are commonly poor in V (e.g., Wan and Yeh 1984; von Knorring et al. 1986).

The PPCC occurrence represents a V- and Cr-rich metamorphic assemblage with goldmanite-uvarovite-grossular garnet, V,Cr-rich clinozoisite, and muscovite. Such V,Cr-rich metamorphic assemblages are very rare. Chromian goldmanite with other V-(Cr)-enriched silicates (titane, allanite, biotite, amphiboles) and variegated V-Cr oxide minerals occur in metasedimentary rocks of the Poblet area, Spain (Canet et al. 2003). Somewhat elevated Cr and Ti contents are reported in vanadium grossular s.s., V,Cr-rich clinozoisite I) indicate the necessity of the peak contact M2 metamorphic conditions resulted in the distinctive enrichment of Mg in the associated mafic silicate minerals and their metamorphic products.

The V-rich metamorphic rocks of the PPCC are closely related to the high organic carbon content. The carbon-rich schists contain, on average, around 2 wt% C styl., 500 ppm V, 100 ppm Cr, 180 ppm Ni, 140 ppm Cu, and 3500 ppm Ti; and locally, up to 6000 ppm V, 1000 ppm Cr, 850 ppm Ni, 530 ppm Cu, and 1 wt% Ti (Table 1; Cambel and Khun 1983). Similar V enrichment and the presence of vanadium garnet and other V-rich silicates has been reported from several C-rich ("black shale") lithologies worldwide (e.g., Filippovskaya et al. 1972; Karev 1974; Litochleb et al. 1985; Benkerrou and Fonteilles 1989; Jeong and Kim 1999; Canet et al. 2003). However, at least a fraction of the V, as well as a main portion of the Cr source originated from the mafic material of the volcanoclastic rocks.

After sedimentation and lithification of the V- and Cr-rich volcano-sedimentary protolith, a complex metamorphic evolution led to the formation of the described mineral association. Three principal metamorphic events can be recognized in the petrogenetic evolution of the V-Cr mineralization in the PPCC (cf. Buday et al. 1962; Korikovsky et al. 1984): (M1) Early Hercynian regional metamorphism of the source material; (M2) Late Hercynian contact thermal metamorphism; (M3) Retrograde effects of M2 and/or Alpine metamorphism.

During the early Hercynian, low-grade greenschist-facies metamorphism (M1) resulted in a fine-grained silicate + carbonaceous matter + pyrite mineral assemblage in the mafic tuffs as well as metamorphic foliation. Subsequent intrusion of the post-kinematic, late-orogenic Modra tonalites to granodiorites into the folded Lower Paleozoic volcano-sedimentary rocks caused late Hercynian, low-pressure contact thermal metamorphism (Korikovsky et al. 1985; Cambel et al. 1989). This dominant metamorphic event was overprinted the regional M1 metamorphism. The M2 event is only locally associated with deformation. The M2 stage was also accompanied by some material input supplied by fluids released from the crystallizing granitic pluton.

The peak contact M2 metamorphic conditions resulted in crystallization of amphibole, diopside, and garnet commonly enriched in V and Cr. Amphibole I porphyroblasts formed simultaneously with diopside, but peak metamorphic conditions led seemingly to the predominance of diopside. Moreover, the presence of rare edenite argues for slightly higher temperature conditions due to their higher Al and Na content in comparison to tremolite-magnesiohornblende (amphibole I) (cf. Laird 1982). Thermodynamic equilibrium was probably not reached among all of the minerals during M2 due to its short duration and the fine-grained structure of the rocks.

Diopside formation can be approximated by the reaction: tremolite + 3 calcite + quartz = 5 diopside + 3 CO₂ + H₂O (Slaughter et al. 1975). Textural and compositional relations among M2 Ca-rich phases (diopside, goldmanite-uvarovite-grossular s.s., V,Cr-rich clinozoisite I) indicate the necessity of a Ca influx or the consumption of carbonates from within the source material.

Minerals associated with the M2 stage are similar to assemblages produced during low-pressure contact thermal metamorphism of common basaltic rocks. For example, the origin of the
two amphibole phases (tremolite-magnesiohornblende and edenite) in association with plagioclase (albite and/or oligoclase to andesine), locally with epidote, chlorite, and quartz, is estimated to have occurred at temperatures between 370 and 450 °C and at least 2 kbar (cf. Maruyama et al. 1983). On the other hand, the crystallization of grossular with V-rich andradite-grossular rims from skarn veins in the Southern Cross greenstone belt, Western Australia, is constrained by the reaction clinozoisite + quartz + calcite = grossular + H₂O + CO₂ to be around 550 °C (Mueller and Delor 1991). In addition, synthetic goldmanite has been prepared experimentally at 530 °C and 3 kbar (Strens 1965).

The youngest metamorphic event M3 clearly shows a retrograde character in comparison to the M2 stage. During M3, a metamorphic association formed under prehnite-pumpelllite facies conditions, which consists of phases low in V and Cr, i.e., pumpellyte-(Mg), muscovite II, clinozoisite II, and prehnite, and possibly albite II and clinochlore II. High hydrothermal quartz + siderite veinlets, also associated with clinozoisite II, points to a metamorphic association formed under prehnite-pumpellite rograde character in comparison to the M2 stage. During M3, Delor 1991). In addition, synthetic goldmanite has been prepared two amphibole phases (tremolite-magnesiohornblende and edenite) in association with plagioclase (albite and/or oligoclase to andesine), locally with epidote, chlorite, and quartz, is estimated to have occurred at temperatures between 370 and 450 °C and at least 2 kbar (cf. Maruyama et al. 1983). On the other hand, the crystallization of grossular with V-rich andradite-grossular rims from skarn veins in the Southern Cross greenstone belt, Western Australia, is constrained by the reaction clinozoisite + quartz + calcite = grossular + H₂O + CO₂ to be around 550 °C (Mueller and Delor 1991). In addition, synthetic goldmanite has been prepared experimentally at 530 °C and 3 kbar (Strens 1965).

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Pan, Y. and Fleet, M.E. (1991) Vanadian allanite-(La) and vanadian allanite-(Ce)
——— (1992) Mineral chemistry and geochemistry of vanadian silicates in
the Hemlo gold deposit, Ontario, Canada. Contributions to Mineralogy and
Petrology, 109, 511–525.
metamorphism of Tatra cover sediments in the Malé Karpaty Mts., Western
Putiš, M. (1987) Geology and tectonics of southwestern and northern part of the
Malé Karpaty Mts. crystalline complex. Mineralia Slovaca, 19, 135–157 (in
Slovak with English summary).
of Lower Paleozoic in the Malé Karpaty Mts. Mineralia Slovaca, 36, 183–194
(in Slovak with English summary).
Sheldrick, G.M. (1997) SHELX-97. Program for the Solutions and Refinement of
Crystal Structures. University of Göttingen, Germany.
of epidote. Doklady Akademii Nauk SSSR, Earth Sciences Section, 185,
1342–1345 (in Russian).
point-dipole model to the problem of optical anomalies in granitide garnets.
siderophile element-rich opaque assemblages from the Leoville carbonaceous
study of equilibria in the system CaO-MgO-SiO2-H2O-CO2. American Journal
of Science, 275, 143–162.
Strens, R.G.J. (1965) Synthesis and properties of calcium vanadium garnet (gold-
Suwa, K., Suzuki, K., Miyakawa, K., and Agata, T. (1979) Vanadian and vanadium
grossulars from the Mozambique metamorphic rocks, Mgama Ridge, Kenya.
Preliminary Reports of African Studies, Nagoya University, 4, 87–96.
pyroclastic rocks of the Malé Karpaty Mts., Western Carpathians, Slovakia.
Canadian Mineralogist, 32, 319–326.
von Knorring, O., Condilffe, E., and Tong, Y.L. (1986) Some mineralogical and
geochemical aspects of chromium-bearing skarn minerals from northern Kar-
Vrána, S. (1966) The veins with axinite and pumpellyite in the Malé Karpaty
Mountains. Časopis pro mineralogii a geologii, 11, 415–421 (in Czech with
English summary).
uvarovites: Part II. Single-crystal X-ray structures. American Mineralogist,
86, 1231–1251.

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