Variation in chemical composition of V-bearing muscovite during metamorphic evolution of graphitic quartzites in the Moravian Moldanubicum

Variace v chemickém složení vanadového muskovitu během metamorfního růstu grafitických kvarců v moravském moldanubiku (Czech summary)

(4 text-figs. 3 tabs)

STANISLAV HOUZAR1 – VLADIMíR ŠREIN2

1 Department of Mineralogy and Petrography, Moravian Museum, Zelný trh 6, 659 37 Brno, Czech Republic
2 Institute of Rock Structure and Mechanics, Academy of Sciences of Czech Republic, V Holešovičkách 41, 182 09 Praha, Czech Republic

Three distinct morphological and paragenetic types of vanadium-bearing muscovite occur as common minor phases in graphitic quartzites in the Moravian Moldanubicum: abundant V-bearing muscovite I (VM1) as green flakes up to 3 mm in size, commonly as intimate intergrowths with graphite and sillimanite; rare V-bearing muscovite II (VM2) as green flakes up to 1 cm in size, exclusively in the ductile quartz-rich nests and veins enclosed in graphitic quartzite; fine-flaked V-bearing muscovite III (VM3) replacing sillimanite I and perhaps also the medium-flaked VM1. Electron-microprobe study gave: 0.03–0.84 apfu V (57.49 wt. % V2O5); 0.05–0.31 apfu Mg (51.52 wt. % MgO); 0.00–0.17 apfu Ti (1.59 wt. % TiO2); VM1 is characterized by high V, Mg and Ti contents; VM2 has low V and Ti, but high Mg concentrations; VM3 shows moderate V, low Ti, but variable Mg. Typical substitutions involve dominant VAl2, and subordinately SiMgAl3, both particularly in the early VM1. Mineral assemblages and textural relationships suggest that the mineral assemblage Qz + Gr + Sili ± V-bearing dravite I is stable if X(H2O) = 0.5 for P < 700 MPa T = 650 °C, and for P > 300–400 MPa T < 570 °C. Mineral assemblages Qz + Kfs ± VM3 ± V-bearing dravite II with VM2 is characterized by elevated activity of O2 and probably H2O (redistribution of graphite and degraphitization). Very low mobility of V during high- to medium-grade metamorphism is evident.

Key words: vanadium muscovite, electron microprobe, metamorphism, graphitic quartzite, Moravian Moldanubicum

Introduction

Graphite-rich rocks and metamorphosed black shales are known to be commonly enriched in a number of trace elements including vanadium (e. g., Vine – Tourtelot 1970). Typical V-bearing minerals include V-bearing micas locally associated with other V-bearing minerals such as dravite, margarite, andalusite and garnets (Snetzinger 1966, Novák – Povondra 1976, Litochleb et al. 1983, Morand 1990, Ankinovitch et al. 1992, Kazachenko et al. 1993). Subordinate silicates and locally also phosphates with variable concentrations of V also were described from graphitic quartzites and gneisses in the Moldanubicum (Bouška et al. 1969, Houzar – Šrein 1993, Houzar 1995, Litochleb et al. 1997), and muscovite is the most abundant carrier of V. Its paragenetic relations, variation in chemical composition, structural properties and substitution mechanisms are discussed here.

Geology and petrography

Quartzites including graphitic quartzites examined are a minor member of the varied rock sequence, consisting of dominant sillimanite-biotite gneiss, leucocratic gneiss, metabasite, and garnet-cordierite migmatite (Jenček et al. 1985). The graphitic quartzites form N-S trending bodies, up to 50 m thick and several hundreds m long, situated in the Moravian Moldanubicum, W of the Třebíč durbachite massif (Fig. 1). Two separated discontinuous belts of graphitic quartzite containing V-bearing minerals are defined: the first stretches from Bílovnáky through

Fig. 1. Map of the occurrences of graphitic quartzites with V-bearing minerals in the Moravian Moldanubicum
1 – granosyenite, 2 – graphitic quartzite with vanadium-bearing minerals
Lesná to Předín (Štěměchy), the second from Jakubov to Čečočovice; an isolated but V-enriched body is located at Řehořov near Jihlava. In the other graphite quartzite bodies known from this region, V-bearing minerals are very rare or absent.

Similar graphite-rich rocks also occur in other parts of the Moldanubicum, e.g. near Černovice, eastern Bohemia (Orlov 1929), Koloděje near Týn nad Vltavou (Bouška et al. 1969), Čučová near Přesek, central Bohemia (Fišera et al. 1982), and Waldviertel, Austria (Holzer 1961, Schrauder et al. 1993).

Graphitic quartzites are dark gray, fine- to medium-grained rocks with significant foliation and locally apparent lineation. Elongated quartz grains significantly predominate over graphite, which forms flakes up to 3 mm in size, locally concentrated around quartz grains, or virtually monomineralic thin bands. Minor minerals include green V-bearing muscovite and sillimanite, both in several distinct morphological and paragenetic types. Two distinct types of V-bearing dravite were recognized at Bítovánky (Houzar – Selway 1997); zircon, apatite and pyrrhotite are common to rare accessory minerals. Mobilized, ductile, graphite-free quartz-rich nests and veins, locally enclosed in graphitic quartzite, are commonly graphite-free and contain K-feldspar, sillimanite, and rare V-bearing muscovite.

Bodies of graphitic quartzite are highly heterogeneous. Thick layers with low contents of V typically containing colourless muscovite (V mostly below detection limit EMP) are interlayered with thin (about 10 cm) V-bearing layers. Vanadium-poor graphitic quartzites also were found in this region but they were not studied in detail. Late, hydrothermal, V-enriched phosphates such as wavellite, variscite, metavariscite and Ba-crandallite associated with quartz and clay minerals were found on late fissures cutting V-enriched layers (Houzar 1995, Sejko-ra et al., 1999).

Chemical composition of graphitic quartzite given in Table 1 shows very high SiO₂ contents about 90 wt. %, C₄v varies from 4.7 to 8.5 wt. %. The concentrations of some trace elements such as V, Cr and Ba are similar to those in carbonaceous rocks of the Bohemian Massif (e.g., Krřbek 1997), and in the graphitic gneiss from Austrian part of the Moldanubicum (Schrauder et al. 1993). The graphic quartzites examined here are apparently enriched in V and depleted in Cr relative to the average black shale (Vine – Tourtelot 1970).

The rock complex containing graphitic quartzites exhibits a rather complicated polyphase metamorphic evolution, common observed in the Moldanubicum: a MP/MT regional metamorphism of a staurolite-kyanite type was mostly overprinted by a LP/HT metamorphic event characterized by the presence of cordierite-sillimanite; migmatization probably related to the younger metamorphic event is locally widespread. A retrograde LP/HT-MT metamorphism is characterized locally by replacement of sillimanite by muscovite (Cháb – Sůk 1977, Vrána et al. 1995).

<table>
<thead>
<tr>
<th>Table 1. Chemical compositions of graphic quartzites</th>
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<tr>
<td>Bítovánky</td>
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</tr>
<tr>
<td>SiO2 wt%</td>
</tr>
<tr>
<td>TiO2</td>
</tr>
<tr>
<td>Al2O3</td>
</tr>
<tr>
<td>FeO</td>
</tr>
<tr>
<td>Fe₂O₃</td>
</tr>
<tr>
<td>MnO</td>
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<tr>
<td>MgO</td>
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<tr>
<td>CaO</td>
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<td>Na₂O</td>
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<tr>
<td>K₂O</td>
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<td>P₂O₅</td>
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<tr>
<td>H₂O</td>
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<tr>
<td>H₂O</td>
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<td>C₄v</td>
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<td>Total</td>
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<td>ppm</td>
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<td>Ba</td>
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<td>Cr</td>
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<td>Cu</td>
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<td>Sr</td>
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<tr>
<td>V</td>
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<tr>
<td>Zn</td>
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<td>Zr</td>
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</table>

Paragenetic and morphological types of V-bearing muscovite

Vanadium-bearing muscovite, the most abundant minor mineral in graphitic quartzites, occurs in three distinct morphological and paragenetic types. V-bearing muscovite I (VM1) is present in graphitic quartzite as green flakes up to 3 mm in size, commonly as intimate intergrowths with graphite and sillimanite I. It seems to be in equilibrium with both latter minerals and possibly also with green V-bearing dravite at Bítovánky (Houzar – Selway 1997). VM1 seems to be the most abundant type widespread at all localities studied (Fig. 1).

Rare V-bearing muscovite II (VM2) forms green flakes up to 1 cm in size, exclusively in the ductile quartz-rich nests and veins enclosed in graphitic quartzite at localities Lesná, Jakubov and Bítovánky. At the last locality, it is also associated with brown V-bearing dravite, K-feldspar and sillimanite II (Houzar – Selway 1997).

Fine-flaked V-bearing muscovite III (VM3) replacing sillimanite I and perhaps also the medium-flaked VM1 is widespread at all localities examined, and it may locally predominate over VM1.

Experimental

Electron-microprobe analyses were performed on a JEOL JXA-50 A instrument at the Geological Institution of the Czech Academy of Sciences, Praha under following conditions: accelerating potential 15 kV, beam current 15 mA, a beam diameter of 2 μm, counting time 20 s. The following standards were used for Kα lines:
leucite (K), diopside (Ca), jadeite (Na), and synthetic compounds for Si, Ti, Al, Fe, V, Mg and Cr. The analytical data were reduced and corrected using the ZAF method.

X-ray diffraction data were obtained with powder Phillips-DRON System (CuKα radiation, 40 kV/40 mA, step scanning 0.02° 2θ, time 2-4 s, internal standard quartz, analyst F. Veselovsky). Data obtained were processed by the X-ray diffraction software ZDS, version 4.81 (P. Ontrade, Czech Geol. Survey).

**Chemical composition, structural and optical properties**

The three morphological and paragenetic types of V-bearing muscovite differ in their chemical composition (Table 2). VM1 is sporadically zoned with V-poore outer zones, other types are rather homogeneous. All types show elevated but variable contents of the roscoelite and celadonite components: 0.03-0.84 apfu V (≤7.49 wt. % V₂O₅); 0.05-0.31 apfu Mg (≤1.52 wt. % MgO), 0.00-0.17 apfu Ti (≤1.59 wt. % TiO₂). Other minor cations include 0.00-0.13 apfu Na, 0.00-0.04 apfu Cr (found only at Bitovanky and Jakubov), 0.00-0.03 apfu Fe and 0.00-0.02 apfu Ba. Variation of some cations are illustrated in Figs 2-4: VM1 is characterized by high V, Mg and Ti contents; VM2 has low V and Ti, but high Mg concentrations; VM3 shows moderate V, low Ti, but variable Mg. Deficiency of interlayer cations (K, Na, Ba) in some analyses, particularly of VM2, may indicate a pres-ence of an illite component commonly reported in some samples of V-bearing muscovite (Johan - Povondra 1988). Typical substitutions in V-bearing muscovite involve dominant Val₁, and subordinate SImGAl₂ or both manifested particularly in the early VM1.

Unit-cell dimensions of muscovite (VM1, VM3) from several localities are given in Table 3; they correspond to the most common muscovite polytype 2M₄.

All types of V-bearing muscovite are dark to light green in a hand specimen as well as in thin sections. They exhibit more or less intensive pleochroism depending on the V content varying from X = pale to light green, Y = Z = yellow-green.

**Discussion**

**Mineral assemblages and PT conditions of their formation**

Mineral assemblages, textural relationships, compositional variation and zonality of the individual minerals (V-bearing muscovite and V-bearing dravite) suggest an apparent polymetamorphic evolution of the graphitic quartzites.

The early mineral assemblage I represented by quartz + graphite + sillimanite I + VM1 (V-poor rim) ± V-bearing dravite I (V-poor core) is volumetrically dominant. Associated bodies of graphite-free quartzite have similar mineral assem-
Table 3. Unit-cell parameters of the vanadium-bearing muscovite samples examined

<table>
<thead>
<tr>
<th></th>
<th>Bitovanky (VM I)</th>
<th>Jakubov (VM I)</th>
<th>Cechohovice (VM I)</th>
<th>Pridlin (VM III)</th>
</tr>
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<tbody>
<tr>
<td>a (10^-6m)</td>
<td>5.204 (3)</td>
<td>5.200 (3)</td>
<td>5.202 (7)</td>
<td>5.208 (2)</td>
</tr>
<tr>
<td>b (10^-6m)</td>
<td>9.001 (6)</td>
<td>8.994 (6)</td>
<td>9.000 (10)</td>
<td>9.009 (3)</td>
</tr>
<tr>
<td>c (10^-6m)</td>
<td>20.12 (10)</td>
<td>20.13 (10)</td>
<td>20.09 (3)</td>
<td>20.10 (9)</td>
</tr>
<tr>
<td>beta</td>
<td>95.57° (1)</td>
<td>95.40° (1)</td>
<td>95.24° (4)</td>
<td>95.68° (9)</td>
</tr>
</tbody>
</table>

1982) as well as high concentrations of V in some minerals very likely enhanced their stability fields (compare Abs-Wurmbach et al. 1982, Guidotti 1984). Relatively low activity of O₂ is likely in such graphite-rich assemblages, whereas graphite-free assemblages indicate elevated activity O₂ (Frost 1979, Labotka 1991).

If XH₂O ≤ 0.5 is assumed (due to abundant graphite), the mineral assemblage I is stable in the area limited by the stability fields of sillimanite and muscovite (Spear – Cheney 1989); for P < 700 MPa T < 650 °C, and for P < 300–400 MPa T < 570 °C. Presence of sporadic kyanite relics in associated graphite-free quartzites, however, indicates that these rocks may previously have reached metamorphic conditions of a kyanite grade. The mineral assemblage II at the ductile, graphite-free, quartz-rich nests with sillimanite, K-feldspar and V-bearing muscovite corresponds to the univariant reaction Ms + Qtz = Kfs + Sill + H₂O. It suggests that the mobilization of quartz and other minerals proceeded at a relatively lower pressure and also at elevated activity of O₂ (Kerrick 1972). However, no concurrent melting is observed in graphitic quartzite.

The zoned distribution of V in muscovite (VM1) (with V-poor rims compositionally similar to those found in VM2), and in dravite I (with V-enriched rims similar in composition to those found in dravite II from ductile quartz-rich nests) was observed at the locality Bitovanky. It may represent a redistribution of V between these minerals during metamorphism. The increase in V contents of dravite relative to muscovite, related to decreasing pressure of metamorphism, indicates that distribution of V between associated mica and tourmaline may have been controlled by pressure. Occurrence of V-rich tourmalines in rocks which underwent low-pressure contact metamorphism (Snetzinger 1966, Kazachenko et al. 1993) supports such idea; however, a systematic study of these relationships at other localities is necessary.

The general model of polymetamorphic evolution and the estimated PT conditions given above are generally consistent with those suggested for the southeastern part of the Moldanubicum by various authors (e. g., Cháb – Suk 1977, Petrakakis 1997).

Mobility of vanadium during metamorphism

Vanadium, generally present as V⁵⁺ in crystal structures of silicates (Schmetzer 1982, Selway et al. 1996) is considered to have very low mobility in metamorphic conditions (Bernier 1990, Par – Fleet 1992). In the graphit-
ic quartzites studied, V may have been originally associated with clay minerals and perhaps with organic matter (e.g., Vine – Tourtlot 1970, Holland 1979, Ripley et. al. 1990). During medium-grade metamorphism, V entered the structure of muscovite (VM1) and locally also dravite. Relatively thin intercalations of contrasting V-rich and V-poor layers characterized by presence of green V-rich or colorless V-poor muscovite, respectively, show that mobility of V was very low during the regional metamorphism M1. Subsequent mobilization of quartz-rich segregations at apparently elevated activity of $O_2$, and probably $H_2O$ caused a partial redistribution (mobility) of V between mica and tourmaline, but on a very small scale. In the same way, the formation of retrograde VM3 at the expense of sillimanite and/or muscovite (VM1) is again restricted to thin V-enriched layers alone. Increasing mobility of V is recorded during formation of late hydrothermal phosphates. However, V is very likely present in $V^{4+}, V^{6+}$ and perhaps also in $V^{4+}$ forms; discussion of this problem is beyond the scope of the present paper. Generally, distribution and chemistry of V-bearing muscovite from graphic quartzites in the Moldanubicum demonstrate very low mobility of V during high to medium-grade metamorphism.

Acknowledgements. The authors thank F. Veselovsky for X-ray study of muscovite, to J. Cempřek for graphic presentations, to M. Novák for helpful comments, and particularly to J. Babrek and P. Černý for critical reading of the manuscript. The work was funded by Granting Agency of the Academy of Sciences of Czech Republic, Grant No. A 3046701.

Submitted October 26, 1999

References


Jenček, V. et al. (1985): Vysvětlivky k základní geologické mapě 1:25 000, list 23 441 Železata, MS, ČÚG Praha.


Variace v chemickém složení vanadového muskovitu během metamorfního vývoje grafitických kvarcitrů v moravském moldanubiku

V grafitických kvarcitech moldanubika na západní Moravě se objevují tři paragenetické typy vanadového muskovitu. První typ (VM1) je reprezentován zelenými lupínky velikosti okolo 3 mm, srovnané s grafitem a sillimanitem. Druhý typ (VM2) tvůrčí až 1 cm velké lupínky v křemenných hnilodech a štítích (asociace Ms + Qz + Kfs + St) v kvarcitu, třetí typ (VM3) je představován drobně šupinatým zeleným muskovitem zasahujícím sillimanit a z části i starší muskovit. Elektronovou mikroanalyzou byly v muskovitu zjištěny zvýšené obsahy vanadu (≤7.49 wt. % V₂O₅), hořčíku (≤1.52 wt. % MgO) a titanu (≤1.95 wt. % TiO₂). Přičemž VM1 má relativně vysoký obsah V, Mg a Ti, VM2 vysoký Mg, ale nízký obsah V a Ti a nejmalší VM3 průměrný obsah V, nízký Ti a variabilní Mg. Dominuje substituce VA₁, a dále SiMgAlᵢ₋ₓ, a to především v nejstarším muskovitu VM1. Minerální asociace i reakční textury v grafitickém kvarcitu odpovídají za předpokladu X⁰ = 0.5 P < 700 MPa a T < 650 °C, a při P < 300–400 MPa a T < 570 °C. Minerální asociace s VM2 je obohacená o grafit a charakterizuje podmínky vyšších aktivit O₂ a pravděpodobně i H₂O, a také nižší tlak. Variace v chemickém složení vanadového muskovitu v metamorfním vývoji studovaných hornin dokumentuje velmi nízkou mobilitu vanadu v podmínkách vysokého až středního stupně metamorfózy.