PETROGRAPHY AND MINERAL CHEMISTRY OF Oligocene Shoshonitic Dacites FROM THE CENTRAL BOSNIA

Salkić Zehra1, Lugović Boško2, Babajić Elvir1

Faculty of Mining, Geology and Civil Engineering, University of Tuzla, Bosnia and Herzegovina
E.mail: salkicz@yahoo.com
2 Institute of Mineralogy, Petrology and Mineral Resources; Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, Croatia

ABSTRACT

Postorogenic volcanic rocks of different Tertiary ages are very common in the Sava-Vardar Zone of the Dinarides and in the southeastern part of adjoining Pannonian Basin. South of the Sava-Vardar Zone, in central Bosnia, Tertiary volcanic rocks occur within ophiolite sequences and genetically related sedimentary formations of the Dinaride Ophiolite Zone. Central Bosnia volcanic rocks are mostly dacites, and highly subordinately andesites as the members of the high-K calc-alkaline series.

It appears from the mineralogical and petrographic characteristics obtained some insight into the processes that occurred during the genesis of the rocks. The presence of primary igneous minerals: clinopyroxene, orthopyroxene, hornblende and biotite from ferromagnesian minerals, and plagioclase, sanidine and quartz, indicates that the fractional crystallization played a significant role in the genesis of the rocks. Reaction edge on many rounded quartz phenocrysts indicates the possibility of magma mixing with the formation of Tertiary volcanic rocks of the central Bosnia. On magma mixing different temperature and chemical composition also indicates the existence of zoned plagioclase and amphibole phenocrysts.

Complex compositional and zoning patterns of biotite and plagioclase phenocrysts and disequilibrium microstructures of plagioclase and quartz phenocrysts suggest interaction of fractionating, mantle derived melts with continental crust during a shallow level pre-eruptive stage and mixing with small amount of devolatilized phlogopite-phyric mafic magma before eruption.

Key words: Oligocene, post-orogenic dacites, petrography, mineral chemistry, central Bosnia

INTRODUCTION

Dacites and subordinate andesites are common in the central Bosnia in the vicinity of Maglaj, Teslić and Nemila (Figure 1). These rocks belong to volcanic formation of shoshonitic and high-K calc-alkaline rocks Oligocene in age. They occur within Tertiary magmatic formation of Dinarides which were successively arising between 55 and 29 Ma genetically related to collision of Apulia (Africa) and Tisia (Euroasia) [1]. On the basis of similar formations and ages, continuation of the collisional zone is recognizable in the Periadriatic Lineament (in the Alps) in the west [2,3] and in the south of the Vardar Zone [4] into the Hellenides [5] and far away in the Taurides [6,7]. The rocks of this formation are the most common in the Sava-Vardar suture zone [8] and, to a lesser extent, in the neighbouring
tectonostratigraphic units [9]. They are associated with granitoids which have, approximately, the same age. It is believed that the magmatic activity is postcollisional and caused by transition from Eocene compressional regime in Early Oligocene transpressional-transtensional tectonic phase [9].

Central Bosnia andesite-dacite rocks have been interpreted to be the oldest Tertiary post-orogenic volcanic rocks of the North Dinarides. Pamić et al. [10] have dated five samples of volcanic rocks in the area of Maglaj and Srebrenica. They proved that analysed rocks, with their K-Ar age of 30.4 – 28.5 Ma, represent the oldest dated postorogenic Tertiary volcanic formations from the North Dinarides. Correlation of data from the North Dinarides with similar rocks from eastern and southeastern Dinarides and North Hellenides suggest that Tertiary volcanic rocks from the central and northeastern Bosnia represent, volumetrically, the most important members of the postorogenic volcanic formations of the SVZ, of the Dinarides and Hellenides [11,12,13].

In this paper petrographical data and mineral chemistry on representative volcanic rocks from the Central Bosnia are reported, and the relationship between petrography and mineral chemistry and the genesis of volcanic are discussed.

Figure 1. Local field relations. Simplified pooled map of Maglaj and area near Teslić

REGIONAL AND LOCAL GEOLOGICAL SETTING

After the Eocene collisional main deformation phase of the Dinarides, continued northward movement of the Apulian block caused dextral transpressional reactivation of the Sava-Vardar suture during the early Oligocene, triggering detachment of the subducted lithospheric slab and extensive shoshonitic magmatism [2,14]. During the Miocene, eastward extrusion of the Alpine-Carpathian Block and rollback of the Carpathian subduction system was accompanied by continued crustal shortening in the
Carpathians and wrench deformation of the internal Dinarides and the Pannonian domain, controlling the subsidence of transtensional and pull-apart basins [15,16,17]. This was coupled with intense thinning of the orogenically destabilized crust and lithospheric mantle of Pannonian Basin, involving upwelling of the asthenosphere [18].

Central Bosnia Tertiary Volcanic Rocks (CBTVR) are situated to the south of the Sava-Vardar Suture Zone (SVSZ) intersecting the thrust sheet of Krivaja-Konjuh ophiolite underlain by genetically related ophiolite mélange of the Dinaride Ophiolite Zone (DOZ) (Figure 1) [19]. Lava extrusions are localized to several volcanic centres situated along deep faults which were a predisposition or channels for the emplacement of Tertiary magmas. Tertiary volcanic rocks of the central Bosnia are the most common in the valley of Bosna river in the area of Maglaj [20,21,22,23], in the vicinity of Nemila near Kolići [20] and ten kilometres westward in the adjacency of Teslić [24].

Dacites in the area of Kolići near Nemila (samples K-1 and K-2) occur within ophiolite mélange as smaller masses, up to about 100 m².

In the area of Maglaj, CBTVR occur within dismembered ophiolites (mainly ultramafics) and genetically related sedimentary formations of the northern marginal parts of the DOZ. There are several smaller volcanic bodies, which together cover an area of a few km². The main body of andesite-dacite rocks, the one from Maglaj, (sample M-5) occur in the contact between ophiolite mélange (mainly shales and graywackes) and the rocks of the Pogari Formation (breccia-conglomerates and sandstones). There are two smaller occurrences, to the north of Maglaj, in the area of Bijela Ploča and Jandrošac. The dacites of Bijela Ploča (sample M-4) occur within peridotites, while andesite-dacite rocks of the Jandrošac quarry are present in the contact between peridotites and the rocks of ophiolite mélange.

CBTVR surrounding Teslić are as small volcanic bodies, surface 50-1500 m², with contacts from various members of Jurassic volcanic-sedimentary formations. To the southwest of Teslić, near Ćuskići, (samples T-2 and T-3), volcanic rocks appear as smaller bodies within Jurassic ophiolite mélange. Dacites were, also, found in the Jasenica brook (samples T-11 and T-14), to the south of Blatnica settlement. Further to the south there are some occurrences which were at the field campaine not safely accessed.

ANALYTICAL TECHNIQUES

Mineral compositions were identified by polarizing microscopy and by X-ray powder diffraction analysis (XRD) using Rigaku X-ray diffractometer at the Institute Maden Tetkik ve Arama (MTA) in Ankara in Turkey.

Minerals were analysed at the Mineralogisches Institut in Heidelberg in Germany with Camebax SX51 microprobe equipped with five wavelength-dispersive spectrometers using an accelerating voltage of 15 kV and a beam current of 10 nA. Natural silicates (albite, orthoclase, anorthite and wollastonite) and oxides (corundum, spinels, hematite and rutile) were used for calibration. Raw data for all analyses were corrected for matrix effects with the PAP algorithm implemented by CAMECA. Calculations of the structural chemical formulas were done by the software package authorised by Hans-Peter Mayer. Additional measurements of minerals were performed by energy-dispersive JEOL JSM 5800 scanning electron microscope at the Institute Jožef Stefan in Ljubljana in Slovenia using an accelerating voltage of 20 kV, peak counting 100 sec, analyzed volume about 1 μm³. EDXS spectra were quantified using SEMQuant program into Link ISIS 300 system.

PETROGRAPHY AND MINERAL CHEMISTRY

The CBTVR are plagioclase, biotite and quartz phric with a micro to cryptocrystalline matrix consists abundantly sanidine and quartz (Figure 3a; Figure 4a and b) along with accessory amount of apatite, hematite, pseudobrookite, zircon, rutile, monazite (Figure 3e and f; Table 1). Samples from
Maglaj eruption center may contain brown glass in the matrix. The rocks are generally fresh and only rocks from Bijela Ploča (sample M-04; Figure 2c) are altered to an aggregate of kaolinite, amorphous silica, dolomite and chlorite.

Table 1. Selected chemical analyses and formulae of accessory mineral from the Central Bosnia Tertiary volcanic rocks

| Sample | K-01 | M-05 | T-14 |
|--------|------|------|------|
| Anal. No. | 15 | 45 | 03 | 04 | 50 | 44 |
| Mineral | Hem | Zrn | Hem | Pbrk | Hem | Mnz |
| SiO₂ | 0.33 | 32.75 | 0.43 | 0.10 | 1.09 | La₂O₃ | 7.23 |
| ZrO₂ | n.d. | 65.81 | n.d. | n.d. | n.d. | Ce₂O₃ | 19.56 |
| TiO₂ | 1.11 | n.a. | 0.77 | 30.68 | 2.25 | Nd₂O₃ | 5.09 |
| Al₂O₃ | 0.38 | n.a. | 0.60 | 0.00 | 0.73 | ThO₂ | 27.69 |
| Fe₂O₃ | 95.36 | 1.54 | 96.09 | 65.97 | 92.05 | Fe₂O₃ | 2.64 |
| FeO | 1.01 | n.d. | 0.57 | 0.00 | 3.31 | CaO | 7.56 |
| MnO | 0.29 | n.d. | 0.52 | 1.61 | 0.00 | SrO | 5.78 |
| NiO | 0.10 | n.d. | 0.12 | 0.50 | 0.01 | P₂O₅ | 24.45 |
| Total | 98.59 | 100.00 | 99.10 | 98.86 | 99.44 | 100.00 |

Table 1 continued...

Zircon and monazite composition analysed by EDS, others by microprobe WDS. Cations calculated on the basis of 3 oxygens and 2 cations for hematite (Hem); 4 oxygens and all Fe as Fe³⁺ for zircon (Zrn); 5 oxygens and all Fe as Fe³⁺ for pseudobrookite (Pbrk); 4 oxygens, all Fe as Fe³⁺ and Ce as Ce³⁺ for monazite (Mnz).

Figure 2. Photomicrographs of the selected dacites and andesites of CBTVR, under crossed polars (N+.2.5x10)

(a) Biotite dacite (sample T-2; locality Ćuskići): large rounded grains of quartz (xenocryst), euhedral biotite phenocrystic and moderately altered plagioclase phenocrystic in holocrystalline matrix

(b) Biotite andesite (sample M-3; Maglaj; Jandrošac quarry): subhedral to euhedral phenocrystics of plagioclase and biotite in hypocrystalline matrix, individual mineral grains are magmatic resorbed.
c) Hydrothermally altered dacite (sample M-4; locality Bijela Ploča): the rock is altered to an aggregate of kaolinite, amorphous silica, dolomite and chlorite; quartz (in the middle) is rounded due to magmatic resorption and contains zircon and rutile inclusions;

d) Hornblende-biotite dacite (sample M-5; Maglaj; below Maglaj fort): euhedral phenocrysts of zonal and twinning plagioclase phenocrysts in holocrystalline matrix.

Table 2. Selected microprobe analyses and formulae of biotites from the Central Bosnia Tertiary volcanic rocks

| Sample | Anal. no. | K-01 | M-03 | M-05 | T-14 |
|--------|-----------|------|------|------|------|
|        | 25c | 26r | 12m | 27c | 2r | 9m | 15c | 16r | 35R | 20c | 27c | 30r | 3m |
| SiO₂   | 36.05| 36.31| 38.31| 35.67| 36.48| 38.30| 39.23| 35.50| 38.84| 37.01| 36.14| 37.98| 37.78 |
| TiO₂   | 3.61 | 3.85 | 2.77 | 3.64 | 3.43 | 3.44 | 2.73 | 3.33 | 2.53 | 3.45 | 3.62 | 3.91 | 3.76 |
| Al₂O₃  | 15.23 | 14.89| 13.92| 15.00 | 14.65| 14.60| 14.81| 16.71| 14.95| 14.59| 15.11| 14.64| 14.77 |
| Cr₂O₃  | 0.00 | 0.00 | 0.02 | 0.04 | 0.00 | 0.01 | 0.34 | 0.00 | 0.32 | 0.00 | 0.03 | 0.00 | 0.00 |
| FeO    | 20.62 | 19.08| 15.76| 19.90| 19.66| 13.46| 8.15 | 18.39| 9.69 | 19.10| 18.53| 14.83| 15.24 |
| MnO    | 0.39 | 0.55 | 0.83 | 0.36 | 0.40 | 0.30 | 0.04 | 0.14 | 0.02 | 0.31 | 0.31 | 0.39 | 0.48 |
| MgO    | 9.76 | 10.57| 14.39| 11.30| 11.61| 15.81| 20.27| 11.34| 20.82| 10.93| 11.64| 13.42| 13.12 |
| CaO    | 0.00 | 0.02 | 0.06 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.10 | 0.25 | 0.14 | 0.21 | 0.06 |
| BaO    | 0.30 | 0.28 | 0.11 | 0.32 | 0.11 | 0.42 | 0.14 | 0.35 | 0.25 | 0.32 | 0.74 | 0.22 | 0.38 |
| Na₂O   | 0.27 | 0.31 | 0.25 | 0.27 | 0.28 | 0.37 | 0.48 | 0.51 | 0.36 | 0.29 | 0.44 | 0.55 | 0.40 |
| K₂O    | 8.96 | 8.93 | 8.43 | 8.61 | 8.65 | 8.24 | 8.79 | 8.47 | 8.10 | 8.73 | 8.63 | 8.64 | 9.06 |
| H₂O    | 3.89 | 3.90 | 3.99 | 3.90 | 3.92 | 4.05 | 4.15 | 3.92 | 4.17 | 3.92 | 3.92 | 4.00 | 3.99 |

Total: 99.07 | 98.68 | 98.84 | 99.02 | 99.19 | 99.00 | 99.13 | 98.66 | 100.15 | 98.90 | 99.24 | 98.80 | 99.03 |

Formulae calculated on the basis of 11 oxygens and total Fe as FeO. H₂O corresponds to stoichiometric 2 (OH) per formula unit. c = phenocryst core, r = phenocryst rim, m = matrix, R = relic in a pseudomorphs after an euhedral microphenocryst. Mg⁸ = 100*[(Mg/(Mg+Fe⁸)].

Quartz is abundant and is mostly confined in the matrix. In all samples quartz occurs as phenocryst which is resorbed and actually represent a xenocryst (Figure 2a and c; Figure 3a and b). Large embayed quartz contain apatite, rutile and zircon inclusions (Figure 2a) and may be jacketed by overgrowths of coticetic sanidine and quartz (Figure 3a and b).

Biotite is common as euhedral dark brown pleochroitic phenocryst and microphenocryst (Figure 2a and b; Figure 3a) which abundantly encases apatite, rutile and zircon inclusions (Figure 3e and f). Some biotite phenocrysts may be slightly altered to aggregate of chlorite, limonite and opaque (Figure 2c). Unaltered phenocrysts and microphenocrysts are continuously reversely zoned (Figure 4a) with discrete across-grain Mg# range of 45.8 - 49.7 for cores and 52.8 - 61.7 in mantles (Table 2).

In the sample M-03 composite mica phenocrysts may show homogeneous phlogopitic core (Mg# ~ 81) overgrown by normally zoned lower-magnesian mantle (Mg# = 56 - 53) that is enriched in Ti and Ba (Figure 4b; Table 2). In the sample M-05 a relic patches of phlogopite (Mg# ~ 79) were identified in an aggregate composed of chlorite, opaque minerals, minor sanidine (Or₉₅₁) and oligoclase (An₄₃₂Or₂₃) (Table 3) representing the pseudomorphs after an euhedral mica microphenocryst (Table 2).

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Hornblende has not been observed although some phenocrysts altered to chlorite, calcite, opaque minerals and minor epidote suggest former hornblende (Figure 2c).

Plagioclase is the principal phenocryst showing euhedral and subhedral crystal forms and twinning (Figure 2d). They often contain apatite, rutile, zircon and biotite inclusions. Some phenocrysts exhibit sericitic replacement, secondary carbonatization (calcite and dolomite) and kaolinization (Figure 2c). Fresh and clear phenocrysts may show normal, reverse and oscillatory zoning patterns even in the same sample (Table 3; Figure 3c; Figure 4c) which witness for recurrent physicochemical disequilibrium within the coexisting magma [25,26].

Some plagioclase phenocrysts are resorbed and due to the fine interconnected melt inclusions may have sieve or dusty textured belts at grain periphery.

Microprobe profiles of some plagioclase phenocrysts show abrupt shifts to more primitive compositions towards the grain margins (Figure 4c).

Overall phenocrystic plagioclase composition ranges from An\textsubscript{48.9} to An\textsubscript{29.9} with the highest calcic compositions mostly confined in the core. Similar compositional range was measured for matrix...
plagioclase (Figure 5) whereby matrix plagioclase compositions mostly match those of phenocryst periphery (Table 3).

Table 3. Selected microprobe analyses and formulae of feldspars from the Central Bosnia Tertiary volcanic rocks

| Sample | K-01 | M-03 | M-05 | T-14 |
|--------|------|------|------|------|
| Anal. No. | 28c | 30r | 34m | 39m | 17c | 18r | 08m | 29m | 25c | 29r | 53m | 09m | 34p | 36p | 35c | 37r | 22m | 24m |
| SrO | 100.66 | 0.610 | 0.002 | 0.000 | 0.317 | 0.004 | 1.373 | 2.633 | 26.24 | 34.9 | 61.8 | 0.57 | 0.14 | 0.09 | 0.15 | 0.30 | 0.16 | 0.36 | 0.00 | 0.22 | 0.18 | 0.06 | 0.33 | 0.04 | 0.12 | n.a. | n.a. | 0.20 | n.a. |
| K2O | 7.08 | 7.37 | 2.28 | 7.39 | 6.38 | 7.03 | 6.33 | 3.16 | 7.04 | 5.68 | 2.90 | 9.51 | 2.17 | 8.26 | 7.14 | 7.12 | 3.37 | 6.81 |
| Na2O | 57.05 | 63.67 | 12.74 | 7.44 | 0.40 | 0.50 | 0.55 | 11.63 | 0.60 | 0.41 | 11.33 | 0.43 | 13.04 | 1.36 | 0.57 | 0.60 | 11.41 | 0.71 |
| Total | 100.66 | 100.18 | 99.11 | 100.60 | 100.72 | 100.91 | 101.06 | 100.68 | 100.89 | 101.00 | 100.37 | 100.72 | 100.25 | 100.95 | 100.42 | 100.83 | 99.55 | 100.16 |
| Si | 2.63 | 2.65 | 2.90 | 2.65 | 2.56 | 2.63 | 2.63 | 2.98 | 2.63 | 2.94 | 2.94 | 2.94 | 2.94 | 2.80 | 2.63 | 2.63 | 3.01 | 2.63 |
| Al | 1.37 | 1.34 | 1.01 | 1.32 | 1.45 | 1.36 | 1.43 | 1.01 | 1.35 | 1.37 | 1.38 | 1.46 | 1.01 | 1.37 | 1.46 | 1.09 | 1.19 | 1.36 | 1.36 |
| Fe2+ | 0.005 | 0.004 | 0.007 | 0.008 | 0.005 | 0.005 | 0.011 | 0.012 | 0.004 | 0.007 | 0.005 | 0.009 | 0.021 | 0.015 | 0.009 | 0.009 | 0.004 | 0.013 |
| Ca | 0.345 | 0.317 | 0.06 | 0.305 | 0.410 | 0.354 | 0.413 | 0.015 | 0.328 | 0.451 | 0.193 | 0.439 | 0.039 | 0.181 | 0.327 | 0.330 | 0.11 | 0.340 |
| Ba | 0.000 | 0.000 | 0.023 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 |
| Sr | 0.002 | 0.003 | 0.002 | 0.004 | 0.008 | 0.004 | 0.009 | 0.000 | 0.006 | 0.005 | 0.001 | 0.008 | 0.001 | - | - | 0.000 | - |
| Na | 0.610 | 0.636 | 0.206 | 0.636 | 0.552 | 0.604 | 0.547 | 0.276 | 0.605 | 0.490 | 0.295 | 0.515 | 0.192 | 0.704 | 0.614 | 0.611 | 0.298 | 0.589 |
| K | 0.032 | 0.036 | 0.757 | 0.042 | 0.023 | 0.028 | 0.031 | 0.670 | 0.034 | 0.023 | 0.655 | 0.024 | 0.759 | 0.076 | 0.032 | 0.034 | 0.665 | 0.041 |
| Total | 5.000 | 5.002 | 4.992 | 4.997 | 5.004 | 4.996 | 5.005 | 4.974 | 4.991 | 4.986 | 4.953 | 4.992 | 4.976 | 4.979 | 4.992 | 4.989 | 4.975 | 4.988 |

Formulae calculated on the basis of 8 oxygens and all Fe as Fe3+. Feldspar end members are in molar %: Or = 100*K/(Ca+Na+K), An = 100*Ca/(Ca+Na+K), Ab = 100*Na/(Ca+Na+K), c = phenocryst core, r = phenocryst rim, m = matrix, p = in pseudomorphose after biotite.

Figure 4. Compositional profiles of 100 × Mg/(Mg + Fe<sup>3+</sup>) and An content across the biotite and plagioclase phenocrysts.
Sanidine is mostly confined to the matrix (Figure 2d; Figure 3d) and minor is found as overgrowths on xenocrystic quartz (Figure 3a). Their overall composition ranges from $\text{Or}_{68.3}$ to $\text{Or}_{81.4}$ without systematic difference in chemistry between these two microtextural types (Table 3; Figure 5).

![Figure 5. Compositional variation in feldspars in diagram Or-Ab-An.](image)

**CONCLUSIONS**

Predominant dacitic rocks of the central Bosnia belong to the Oligocene volcanic formation of the shoshonite and high-K calc-alkaline rocks. This formation is a member of Tertiary magmatic formations which were successive originating between 55 and 29 Ma genetically related to the collision of Africa and Euroasia in the Dinaridic segment.

On the basis of optical investigations, XRFA and XRDA data it is affirmed that the dacites dominate over the andesites. According to prevailing content of ferro-magnesium minerals the following varieties of the the rocks can be distinguished: biotite dacites (Kolići, Teslić, Maglaj), hornblende-biotite dacites (Maglaj) and biotite andesites (Maglaj). The rocks mostly have holocrystalline porphyritic texture with phenocrysts of plagioclase, sanidine, quartz, biotite, subordinate amphibole and very rarely orthopyroxene. The same minerals are, also, present in the matrix together with accessories (apatite, zircon, rutile, monazite and magnetite). Microscopic observations show that zircon becomes more abundant than magnetite and ilmenite as the igneous rocks become more evolved.

From the petrographic characteristics and mineral chemistry it is obvious that magma mixing played significant role in the evolution of the CBTVR. Some of quartz phenocrysts show dense reaction rims and resorption textures. It means that a large grains of quartz are magmatic resorbed and corroded, and indicates disequilibrium with coexisting magma. Such features suggest either they are xenocrystals entrained into the magma from crustal rocks or they have been fractionated from acidid magma which mixed with less evolved magma.

Beside resorbed quartz phenocrysts, plagioclase phenocrysts may show inverse zoning and signs of resorption. Early formed plagioclase phenocrysts crystallized under AFC (assimilation and fractional crystallization) conditions close to the roof of the chamber and were subsequently entrained in a liquid
mixture composed of evolved interstitial liquid held in the partly crystallized roof zone and newly injected parental magma.

Similar reaction often affected numerous amphibole phenocrysts (?). The presence of zoned plagioclase and resorbed amphibole phenocrysts can also be caused by changes in intensive parameters such as pressure or volatile affecting during the magma’s rise to the surface. Pseudomorph after biotite consisting of fine-grained oxides and silicates. Similar reaction products of biotite in dacites were interpreted by Nixon [27] as resulting from dehydration above its stability limit attending magma mixing.

From the petrographic and chemical properties, it is evident that magma mixing and “association” have played a significant role in the evolution of CBTVR. Petrographic evidences (imbalance in texture) are: the sieve edges of plagioclases, normal and fine plagioclases in the same specimen, rounded and round quartz; reactive edge on biotite and pseudomorphoses by mafic phases.

(Received February 2020, accepted February 2020)

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