Major and trace element composition of olivine from magnesian skarns and silicate marbles

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Abstract

Olivine is a major rock-forming mineral in various magmatic and metamorphic rocks and upper mantle. In this paper, we present first high-precision analyses of olivine from 15 samples of magnesian skarns and silicate marbles (MSSM) from the collection of the Fersman Mineralogical Museum (Moscow, Russia). Mg# (Mg/(Mg+Fe²⁺)*100, mol.%) of olivine from the samples studied varies from 86 to nearly 100. The main distinctive features of the olivine are anomalously low contents of Co (<51 µg/g), Cr (< 5 µg/g) and Ni (< 44 µg/g) and high content of B (23-856 µg/g), which correlate with host-rock compositions. Phosphorus (5-377 µg/g) incorporation in olivine is charge-balanced by the incorporation of Li (0.15-61 µg/g) and Na (<14.3 µg/g). Y and REE contents exhibit positive correlations with Na, which suggest that REE
incorporation into MSSM olivine could occur via charge-balanced coupled substitution with Na at low temperature and low $a$SiO$_2$ conditions during MSSM formation. The documented compositional features of olivine from magnesian skarns and silicate marbles can help reconstruct the genesis of the host-rocks and identify xenocrysts of MSSM olivine in magmatic rocks.

**Keywords:** Olivine; LA-ICP-MS; magnesian skarn; silicate marble; contact metamorphism

**Introduction**

Calc-silicate metamorphic and metasomatic rocks, mantle peridotites and mafic igneous rocks are three major rock types of common occurrence of magnesian olivine (Mg$\#>$80 after Plechov et al. (2018)). Olivine-bearing calc-silicate metamorphic and metasomatic rocks are represented by magnesian skarns and silicate marbles (hereafter referred to as MSSM). MSSM have similar mineral assemblages, which include carbonates (calcite or dolomite), olivine, phlogopite, diopside, spinel, periclase, clinohumite, and pargasite. Magnesian silicate marbles are difficult to distinguish from magnesian skarns by mineralogy or chemistry. The only major difference between them is their geological position. Magnesian skarns are the product of contact metasomatism and always located in the aureoles of magmatic intrusives (Zharikov et al., 2007), whereas olivine-bearing magnesian silicate marbles are not associated with magmatic rocks. Olivine-bearing magnesian silicate marbles could form during high-grade metamorphism or infiltration metasomatism of dolomites (Bucher and Grapes, 2011). Olivine-bearing MSSM can form in wide range of pressures (from ~1 to ~10 kbar) and temperatures (from ~550 to ~900 °C) as follows from thermodynamic estimates (Bucher and Grapes, 2011; Pertsev, 1974; Zharikov, 1970). The majority of temperature and pressure estimates for olivine growth in carbonate-silicate metamorphic or metasomatic rocks lies in the ranges of 550-700°C and 0.5-5 kbar, for example: about 600°C and from 1 to 5 kbar for
Tazheran, Russia (Doroshkevich et al., 2017), 595 °C and 1.8±0.5 for Twin Lakes pendant, California, USA (Ferry et al., 2011), 680 °C and 0.5 kbar for Beinn an Dubhaich aureole, Isle of Skye, Scotland (Ferry et al., 2011), and 550 °C and 2.5 kbar for Gruvaisen, Sweden (Hellingwerf, 1984).

The concentration ranges of major, minor and trace elements in igneous and mantle olivines that are formed at higher temperatures and wider range of pressures are increasingly well-characterized (e.g. Arai, 1994; Bussweiler et al., 2019; De Hoog et al., 2010; Foley et al., 2013; Jaques and Foley, 2018; Neave et al., 2018; Rooney et al., 2020; Sobolev et al., 2007; Sobolev et al., 2008; Su et al., 2019; etc.), whereas high-precision data on the composition of olivine from MSSM are very scarce. These published data include several ion probe analyses of B-rich olivine from the Tayozhnoye deposit (Grew et al., 1991), high-precision electron probe analyses of olivine from Kuh-i-Lal deposit (Plechov et al., 2018), some routine (non-high-precision) microprobe analyses of olivine from Tazheran deposit (Doroshkevich et al., 2017), Twin Lakes pendant (California, USA) and Beinn an Dubhaich aureole (Isle of Skye, Scotland) (Ferry et al., 2011) and from primitive magmatic skarns found as xenoliths in magmatic rocks (Fulignati et al., 2005; Gilg et al., 2001; Wenzel et al., 2002). These published data are too scarce to place constraints on the entire variations of olivine composition from MSSM.

In this work we systematically study the content of major, minor and trace elements in olivine from MSSM from different locations. The new data reveal distinctive compositional features of olivine from these rocks, which are manifested in strong enrichment in B combined with depletion in Ni, Co and Cr concentrations in comparison with typical igneous and mantle olivine.

Samples and methods

We studied a total of 15 samples of magnesian skarn (or silicate marbles in some cases) olivine from nine different locations in three countries (Table 1, Fig. 1) from the collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences (Moscow, Russia).
samples are representative of both magnesian skarns and silicate marbles. The samples of magnesian skarns are from three classical localities: Nikolai-Maximilian mine, South Urals, Russia (e.g. Bocharnikova et al., 2011), Slyudyanka, Baikal area, Russia (e.g. Aleksandrov and Senin, 2006) and Kukhilal, Tajikistan (Pautov et al., 2018). The sample from Belaya Vyemka, Baikal area, Russia, is a spinel-forsterite marble (Sal’nikova et al., 2007). Five samples are selected from contact zones of carbonate rocks with alkaline intrusives (Tazheran, Russia, and Hodzha-Achkan, Kyrgyzstan) (e.g. Doroshkevich et al., 2017; Pautov et al., 2013) and another five samples are from skarns of phlogopite deposits in Yakutia, Russia, (Katalakh, Emeldhak and Timpton) associated with granites (e.g. Mikhailov, 1997).

High-precision electron microprobe analysis (EPMA) of studied olivine samples was conducted using a wavelength-dispersive X-ray (WDS) electron microprobe JEOL JXA-8230 (Lomonosov Moscow State University) operated at an accelerating voltage of 20 kV and a beam current of 100 nA. San Carlos olivine USNM-111312/444 (Si, Mg, Fe), metal oxides (Ti, Mn, Cr, Al, Ni), wollastonite (Ca) and Durango apatite (P) were used for calibration. The peak signal accumulation time was 120 s for Cr, Ti, P, Mn and Ni, 180 s for Al, 40 s for Ca, respectively. Analysis at high beam current and long counting times significantly lowers detection limits of trace element in olivine (Sobolev et al., 2007). Analytical precision, which was determined as 2 standard deviations of multiple repetitive analyses of San Carlos olivine (USNM-111312/444), was estimated to be 41 µg/g for Ni, 33 µg/g for Mn, 9 µg/g for Ca, 11 µg/g for P, 12 µg/g for Al, 19 µg/g for Cr and 8 µg/g for Ti. The results are presented in Supplementary Table 1. San Carlos olivine (USNM-111312/444) was used as a secondary standard (Supplementary table 4).

Major and trace element concentrations of the same olivine samples were also analyzed by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) using an Agilent 7900s quadrupole mass-spectrometer coupled with the 193 nm Excimer Laser-Ablation system GeoLas™ HD (Coherent) at the Institute of Geosciences, Kiel University. Instrumental conditions, mass numbers analyzed, and details of data reduction are given in Supplementary
Table 5. In brief, the analyses were performed using two volume ablation cell (ETH Zürich, Switzerland; Fricker et al., 2011) with a carrier gas flow of 0.7 L min$^{-1}$ He and addition of 14 mL min$^{-1}$ H$_2$. The carrier gas was mixed with Ar ($\sim$1 L min$^{-1}$) prior to introduction to the ICP-MS. The ablation was done with laser beam diameter ranging from 32 to 120 µm, pulse frequency of 10 Hz and fluence of 5 J/cm$^2$. Every analysis comprised 20 s background measurement (laser-off) and 40 s of signal measurement (laser-on). The initial data reduction was performed in the GLITTER software (Griffin et al., 2008). The intervals for integration of analytical signal were manually defined to avoid possible contamination by inclusions in olivine, which are usually detectable by strongly elevated concentrations of highly incompatible elements (K, Rb, U, Pb etc.). The data were initially quantified using glass KL2-G (Jochum et al., 2006) obtained using laser spot of 120 µm and Si as reference element, assuming SiO$_2=40$ wt% in olivine. A secondary standard of olivine MongOL Sh11-2 (Batanova et al., 2019) was used for minor matrix and spot size correction of concentrations of Si, Mg, Fe, Li, Na, Al, P, Ca, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Sr, Y, Zr, Dy, Ho, Er, Tm, Yb and Lu (Supplementary Table 3). A correction was applied for the $^{29}$Si$^{16}$O interference on $^{45}$Sc by analysis of synthetic nominally Sc-free quartz analysed throughout the measurement session. The final step was proportional adjustment of all concentrations to obtain the sum of SiO$_2$, TiO$_2$, Al$_2$O$_3$, FeO, MnO, MgO, CaO, Na$_2$O, K$_2$O, NiO, Cr$_2$O$_3$, P$_2$O$_5$, ZnO, and V$_2$O$_3$ equal to 100 wt%. The results are presented in Supplementary Table 2.

Eight elements in olivine were measured both by EPMA and LA-ICP-MS methods: Si, Fe, Mg, Ti, Al, Mn, Ca, P. Comparison of the data obtained with ca. 5 µm (EPMA) and 32-120 µm (LA-ICP-MS) spots is instructive about the existence of a small scale compositional heterogeneity of the samples. Statistical analysis of this comparison (Ludwig, 1980; York et al., 2004) shows that the linear regressions for Mg#, Ti, Mn and P do not significantly differ from the line of equal concentrations (1:1 line). MSWD is less than 1.8 for Ti and P, which means that the two analytical methods give statistically indistinguishable results for these elements with probability...
of 95% (Wendt, Carl, 1991; Fig. 2). High MSWD for Mg# and Mn can be explained by some
compositional heterogeneity of the samples, exceeding the analytical precision. There is minor
systematic difference between the EPMA and LA-ICP-MS data for Ca, which exceeds 2
standard deviations and is probably linked to O\(^-\), OH\(^-\) and N\(^-\) based interferences from Mg and Si
on minor isotope of \(^{43}\)Ca used for LA-ICP-MS analysis (e.g. Batanova et al., 2019). Therefore,
EPMA data for Ca were preferred in this study. Significantly higher concentrations of Al
obtained by EPMA (Fig. 2) on some samples can result from contamination of olivine surface by
Al\(_2\)O\(_3\) used for polishing (e.g. Batanova et al., 2015). LA-ICP-MS analyses appear to be free of
this problem and were used in our study.

**Results**

**Petrography**

MSSM samples studied are represented by olivine-calcite-spinel (Fig. 3a), olivine-calcite-
phlogopite (Fig. 3b) and olivine-calcite-spinel-phlogopite (Fig. 3c) mineral associations.
Diopside and amphiboles are also occur in some samples as rock-forming minerals. Most
samples are unaltered. The primary rock textures are granoblastic and grano-porphyroblastic.
Proportions of rock-forming minerals in studied samples vary widely. In general, calcite makes
up more than 50 vol.% in most of them, olivine – up to 50 vol.% , while the contents of spinel
and phlogopite are rarely exceed 20 vol.% of the rocks. Olivine in these samples has idiomorphic
shape and size ranging from 0.1 to 2 mm. Some samples (74607, 67723, 67792, and 77329) are
strongly serpentinized (up to 90 % of olivine). Olivine in these samples occurs as relics in the
serpentine matrix (Fig. 3d). Many olivines studied contain crystal inclusions of the other rock-
forming minerals and also accessory minerals such as apatite, pyrrhotite, magnetite and ilmenite.
Some olivine grains contain abundant fluid inclusions.

**Olivine Mg#**

Mg# of studied olivine samples varies from 86.3 to 99.8, assuming all measured Fe as Fe\(^{2+}\). Only
four studied samples have Mg# < 95, which overlaps with Mg# of typical olivine from mantle
xenoliths and magmatic rocks (e.g. De Hoog et al., 2010; Sobolev et al., 2007; Su et al., 2019). The other samples are more Mg-rich (Fig. 4). The high-Mg composition of the studied olivine samples is in a good agreement with the previous descriptions of olivine from magnesian skarns (e.g. Plechov et al., 2018; Zharikov, 1970). It should be noted that extremely high-Mg olivine (Mg#>96) can also occur in magmatic rocks (Blondes et al., 2012; Bussweiler et al., 2015; Plechov et al., 2018). However, these olivines are usually interpreted to result post-magmatic processes like oxidation and low-temperature re-equilibration. Some of these previously reported ultra Mg-rich olivines can also be xenocrysts from skarns.

**Minor elements (Al, Ca, Mn, Ni, Co, and Cr)**

As minor elements we here consider elements which occur in olivine at concentrations < 10,000 µg/g and are typically measured by EPMA in other studies (e.g. Sobolev et al., 2007), i.e. Al, Ca, Mn, Ni, Co and Cr. Some of these elements (e.g., Co, Cr and Al) have concentrations below the detection limit of EPMA in the studied olivine, thus they were analyzed by LA-ICP-MS.

Contents of Al, Ca and Mn in the studied olivine samples vary widely: Al – from 0.5 to 108 µg/g; Ca – from 40 to 1880 µg/g; Mn – from 140 to 4140 µg/g (Fig. 4). The contents of Ca and Al do not show any correlation with the olivine Mg# and largely overlap with the typical values for mantle olivine (Fig. 4). Mn content in studied olivine reveals clear negative correlation with Mg#, which is also a typical feature for olivine of magmatic and metamorphic genesis (e.g. De Hoog et al., 2010; Sobolev et al., 2007; Su et al., 2019). Some of studied MSSM olivines with Mg# of ~88 contain twice as much Mn as the most Mn-rich igneous olivine (Fig. 4). Average Mn/Fe*100 of MSSM olivine is ~5.3, which is significantly higher than typical values for igneous and metamorphic olivine (~0.5-2) (De Hoog et al., 2010; Sobolev et al., 2007; Su et al., 2019). However, Mn/Fe*100 ranges from 1.4 to 20 for different studied samples (Fig. 4) making it difficult to discriminate olivine formed in different environments solely on the base of this parameter.
Relative variations of Ni (0.2 - 44 µg/g) and Co (0.3 - 51 µg/g) contents in studied olivine are even larger than for Al, Ca and Mn. The contents of both these elements correlate negatively with Mg# (Fig. 4). However, even the highest Co and Ni contents in olivine from MSSM do not reach the lowest content of these elements in high-Mg# olivine of mantle and magmatic origin (e.g. De Hoog et al., 2010; Sobolev et al., 2007; Su et al., 2019). Variations of Cr content in the studied olivine samples are the smallest – from 0.5 to 4.9 µg/g. The contents do not correlate with olivine Mg# and are lower than in high-Mg# olivine of mantle and magmatic genesis (Fig. 4).

Trace element contents in olivine

Significant amounts of Li, B, Na, Sc, V, Cu, Zn, Sr, Y, Zr, Dy, Ho, Er, Tm, Yb and Lu were detected in the studied olivine samples by LA-ICP-MS (Supplementary Table 2). Li content varies from 0.15 to 61 µg/g and shows a positive correlation with the content of P, which varies from 5 to 377 µg/g (Fig. 5a). Y (<1.3 µg/g), Dy (<0.04 µg/g), Ho (<0.03 µg/g), Er (<0.22 µg/g), Tm (<0.08 µg/g), Yb (<1.1 µg/g) and Lu (<0.31 µg/g) reveal clear positive correlations with Na content (from 0.15 to 14 µg/g) (Fig. 6).

Ti content varies widely from 3.7 to 159 µg/g and does not correlate with Mg# or the contents of other elements. On average, Ti in studied MSSM olivine has nearly the same content as olivine from magmatic rocks and mantle xenoliths (Fig. 7a). Boron content in studied MSSM olivine ranges from 23 to 856 µg/g and similarly to Ti does not correlate with Mg# or with contents of other elements. This B content is 2-3 orders of magnitude higher than in olivine from mantle xenoliths (Fig. 7b).

Zn in studied MSSM olivine samples has a similar distribution pattern as Mn. Zinc contents for most of studied olivine samples exhibit a clear negative correlation with Mg# and increases from 5-10 µg/g at Mg#99.8 to ~380 µg/g at Mg#86-88, which is higher than in olivine with similar
Mg# from igneous and mantle rocks (De Hoog et al., 2010; Kamenetsky et al., 2018; Nekrylov et al., 2018; Neumann et al., 1999; Savelyev et al., 2018; Su et al., 2019) (Fig. 7c). The exceptions are olivine samples PB-15/3, 75567 and 67792, which do not show any dependence of Zn content on Mg#, and all have Zn content below 20 µg/g. Fe/Zn ratio in studied olivine varies from ~300 to ~3000, which covers the range of Fe/Zn in olivine from igneous and mantle rocks (mostly 1000-2000) (Fig. 7c). The measured contents of Sc (0.4-30 µg/g), V (0.03-3.3 µg/g), Cu (up to 0.3 µg/g) and Zr (0.05-17.7 µg/g) do not show any clear distribution patterns.

Discussion

Comparison of olivine from MSSM, magmatic rocks and mantle peridotites

Magmatic rocks often contain olivine xenocrysts of questionable origin (e.g. Brett et al., 2009; Chayka et al., 2020; Plechov et al., 2017 etc.). Reliable discrimination of the olivine provenance should be based on high quality reference chemical data. Such data exist now for olivine from magmatic silicate rocks (e.g. Foley et al., 2013; Jaques and Foley, 2018; Neave et al., 2018; Sobolev et al., 2007 etc.) and from mantle peridotites (e.g. Bussweiler et al., 2019; De Hoog et al., 2010; Foley et al., 2013; Su et al., 2019). The composition of olivine from high-Mg metamorphic rocks is very poorly known that hampers its identification using chemical criteria.

Studied olivine from MSSM has some distinctive features, which can be used to discriminate it from magmatic and mantle olivine. The most prominent feature is low content of Co (<51 µg/g), Cr (< 5 µg/g) and Ni (< 44 µg/g) in comparison with olivine of the same Mg# (> 85) from mafic magmatic rocks and mantle xenoliths (Fig. 4). This compositional feature is likely related to low Co, Cr and Ni content in sedimentary dolomites (e.g. Carmichael et al., 2008; Ephraim, 2012; Weber, 1964), which are common protoliths for MSSM.

Another distinctive feature of olivine from MSSM is high content of B (23-856 µg/g). Boron content in olivine of other origins is poorly known. The available data indicate concentrations of <0.5 µg/g in olivine from mantle xenoliths (with one anomalous grain containing 67 µg/g) (e.g.
Kaliwoda et al., 2008; Kent and Rossman, 2002), <21.5 µg/g in olivine from highly metasomatized mantle veins in sub-arc mantle (Bouilhol et al., 2009), <8 µg/g in subcontinental lithospheric mantle (Chayka et al., 2020), <23 µg/g in olivine from high-pressure serpentinites (De Hoog et al., 2014), <11 µg/g in olivine from kimberlites and lamprophyres (Nosova et al., 2017; Nosova et al., 2018), <165 µg/g in lamproites (4 ± 3.5 µg/g without one anomalous olivine crystal) (Chayka et al., 2020), ~4 µg/g in olivine from Stapafell tholeiite (Jeffries et al., 1995), ~12 µg/g in olivine from Hawaiian ankaramite (Jeffries et al., 1995) and <1 µg/g in arc-related magmatic olivine from South Sulawesi (Elburg et al., 2006). All of these data suggest that the observed concentrations of B content in MSSM olivine are anomalously high in comparison with olivine from other environments. Our results are in a good agreement with previously reported data on B enrichment in olivine from magnesian skarns (Grew et al., 1991; Sykes et al., 1994). This compositional feature of olivine from MSSM is also likely linked to the compositions of their protoliths – dolomites, which are strongly enriched in boron (Harder, 1970; Weber, 1964) relative to mafic magmatic and mantle rocks. Such enrichment is caused by the lithophile behavior of boron and its high solubility in aqueous fluids and enrichment in seawater (e.g. Grew, 2015), which makes it abundant in marine sediments.

The new data on the composition of MSSM olivine can be used now to place constraints on the origin of some previously enigmatic olivine xenocrysts of magmatic rocks. For example, we can now discuss the origin of extremely high-Mg olivine (Mg#>96) from lavas of Pian di Celle volcano, Italy (Plechov et al., 2017). In our previous study we argued that this olivine is unlikely of magnesian skarn origin because of low Mn and Ca content, not correlating with the composition of host rocks (Plechov et al., 2018). This interpretation requires revision in light of our new data. It is evident from our new data that low Mn and Ca contents of extremely high-Mg olivine described in lavas of Pian di Celle volcano are in fact typical for olivine with Mg# > 98 from MSSM. This implies that typical metasomatic MSSM olivine can occur as xenocrysts in
volcanic rocks as well as olivine from primitive magmatic skarns (Fulignati et al., 2005; Gilg et al., 2001; Wenzel et al., 2002).

Wang et al. (2020) have recently described an olivine-rich rock, which they called “jianite”. This rock of uncertain origin was found among various Proterozoic felsic volcanic rocks and marbles of Mayihe formation (Ji’an County, Jilin Province, Northeast China) (Wang et al., 2020). LA-ICP-MS analyses of the olivine from “jianite” revealed extremely high content of B (1763 ± 23 µg/g) and low contents of Cr (0.92 ± 0.08 µg/g), Co (0.58 ± 0.03 µg/g) and Ni (0.91 ± 0.06 µg/g) (Wang et al., 2020). Our new data strongly suggest a MSSM-related origin of this olivine. Therefore, we suggest that jianites represent altered olivine-rich magnesian skarns.

**Occurrence of low-Ca olivine and monticellite in MSSM**

Olivine from MSSM might be expected to have high Ca content, because CaO is a major component for these rocks, which mainly contain more than 50 vol.% of calcite. However, olivine studied in our work has rather low Ca content (40-1880 µg/g), which is similar to Ca content in olivine from mantle peridotites and significantly lower than Ca content in olivine from magmatic rocks (Fig. 4). It is however important to note that MSSM do not necessarily contain low-Ca olivine; some of them host pure monticellite (MgCaSiO₄). Both low-Ca olivine and monticellite occur in common MSSM association with calcite, spinel, phlogopite and diopside, sometimes in the same samples (Tracy et al., 1978, Wenzel et al., 2002). Thus, there is no obvious host-rock compositional control on the crystallization of monticellite or olivine in MSSM; both minerals appear to crystallize at relatively high CaO activity in fluid in contact zones of magmatic intrusions and carbonates.

Stability of monticellite or olivine can be described via the following reaction: 2MgCaSiO₄ +2CO₂ = Mg₃SiO₄ + 2CaCO₃ + SiO₂. According to this reaction, there can be also compositional control on the stability of these olivine polymorphs in MSSM. Crystallization of low-Ca olivine in association with calcite should be favored at high fCO₂ and low aSiO₂. In opposite,
monticellite should be more stable at lower \( f\text{CO}_2 \) and in more SiO\(_2\) rich systems, for example, during low-pressure (<1.5 kbar) contact metamorphism of clay-rich limestones.

In addition to system composition, temperature has important control on the incorporation of Ca in olivine, promoting crystallization of more Ca-rich olivine with increasing temperature (e.g. Adams, Bishop, 1982, Shejwalkar, Coogan, 2013). It is thus likely that the occurrence of monticellite or olivine is also controlled by the temperature of skarn formation so that low-Ca olivine forms at low temperature (generally <700 °C) and is replaced by monticellite at higher temperature (e.g. Fig. 112 in Zharikov, 1970). Indeed some empirical data support this view as monticellite is usually found closer to the contact of scarns with intrusive body (Sinyakov, 1961).

Although more strict thermodynamic analysis is required to more precisely determine the conditions of olivine crystallization in MSSM, our data allowed us to place semi-quantitative constraints on these conditions. We propose that the paradoxically low Ca content in MSSM olivine may reflect specific conditions of the olivine origin, which is crystallization from a CO\(_2\)-rich fluid at low-temperature and low \( a\)SiO\(_2\). The olivine is replaced by monticellite at higher temperature, lower \( f\text{CO}_2 \) and at higher \( a\)SiO\(_2\). This conclusion is in well agreement with the previously published data and thermodynamic modelling on the conditions of MSSM formation (e.g. Bucher and Grapes, 2011; Pertsev, 1974; Zharikov et al., 2007).

### Incorporation of trace elements in MSSM olivine

The observed positive correlation of P and Li (Fig. 5a) is in a good agreement with the charge-balanced coupled substitution \( \text{IV} \text{Si}^{4+} + \text{VI}(\text{Fe}, \text{Mg})^{2+} = \text{IV} \text{P}^{5+} + \text{VI} \text{Li}^{+} \) (Buseck and Clark, 1984; Woodland et al., 2004). Sodium content reveals a weaker positive correlation with the content of P (Fig. 5b) than that of Li. However, a similar reaction could be the main mechanism of Na incorporation into the olivine structure (Mallmann et al., 2009). Indeed, molar Li + Na content nearly balance the P content for most of the studied olivine samples from MSSM (Fig. 5c).
Relatively high MSWD value for molar P and Li+Na 1:1 line suggest that there are most likely involved other mechanisms of P incorporation into the olivine structure along with this one. Excess of P relative to Li and Na observed in some samples (Fig. 5c) can be balanced by the octahedral vacancies via reaction $2^{IV}Si^{4+} + ^{VI}(FeMg)^{2+} = 2^{IV}P^{5+} + ^{VI}(vac)^{0}$ or trivalent cations such as Cr, Al, Fe$^{3+}$ or even REE via reaction $^{IV}Si^{4+} + ^{VI}(FeMg)^{2+} = ^{IV}P^{5+} + ^{VI}(Cr, Al, Fe, Sc, REE)^{3+}$ (e.g., Milman-Barris et al., 2008; Shchipalkina et al., 2019; Shea et al., 2019). However, we found no significant correlation of the P excess with the amount of trivalent cations in MSSM olivine. Therefore, we propose that the former reaction involving octahedral vacancies is the most likely mechanism for the incorporation of the P excess in the MSSM olivine.

The prevailing mechanisms of REE and Y incorporation in olivine structure is a matter of long-year discussion. In a recent study, Burnham and O’Neill (2020) concluded that these elements replace Mg$^{2+}$ on octahedral sites, but with charge-balance achieved by two different mechanisms: (1) cation vacancies (2 REE$^{3+}$ + vacancy = 3 Mg$^{2+}$); and (2) substitution of Al for Si (REE$^{3+}$ + Al$^{3+}$ = Mg$^{2+}$ + Si$^{4+}$). These results confirm conclusions of previous studies (e.g. Colson et al. 1989; Beattie, 1994; Di Stefano et al., 2019; Spandler and O’Neill, 2010), but show that REE can enter olivine simultaneously using different mechanisms, depending on SiO$_2$ and Al$_2$O$_3$ activity in the system.

Alternatively it was suggested on the basis of thermodynamic calculations that REE substitution on the octahedral site can be charge-balanced by monovalent cations via reaction $2^{VI}(Fe, Mg)^{2+} = ^{VI}(H, Li, Na)^{+} + ^{VI}(Y, REE)^{3+}$ (e.g., Colson et al, 1989). The coupled substitution of 2Mg with REE and proton in olivine (REESiO$_3$(OH)) has been shown by Berry et al. (2007). Coupling with Li was not considered as important mechanism because of low Li abundance in most olivine-bearing rocks. The mechanism involving Na has been proposed as potentially significant (e.g., Burnham, O’Neill, 2020), but it was not studied experimentally in sufficient details thus far.
Our data show general positive correlation of Y+REE and Na contents in MSSM olivine (Fig. 6). This correlation may suggest that Na-rich fluids, from which the olivine crystallized, are also enriched in REE+Y, and thus this correlation reflects the compositional peculiarity of fluid composition. On the other hand, the correlation may also suggest the coupled incorporation of REE+Y and Na in MSSM olivine. Because only ~ 2 % of all Na atoms in olivine are required to charge-balance REE+Y content in olivine (Fig. 6), this mechanism does not contradict the previous conclusion about the coupled P, Li and Na incorporation into the MSSM olivine structure.

Although the exact mechanisms of REE+Y incorporation in MSSM olivine are uncertain, we propose that the coupled substitution of REE+Y with monovalent cations, particularly with Na and H, as well as coupled substitution with Al in tetrahedral site may be important in low temperature hydrothermal environment, where olivine crystallize from CO$_2$-H$_2$O fluid at low SiO$_2$ activity. In contrast, the mechanism involving cation vacancies is likely more important at high SiO$_2$ activity in magmatic systems.

**Conclusions**

We present results of a systematic study of major, minor and trace elements contents in olivine from MSSM. A total of 15 olivine samples originate from nine different locations in three countries and are part of the collection of the Fersman Mineralogical Museum RAS (Russia). Our data allowed us to place constraints on the compositional variations of this olivine, highlight its distinctive features and provide new insights on the incorporation of trace elements in the olivine structure. Our main conclusions are the following:

1) Mg# of MSSM olivine varies from ~ 86 to nearly 100. The olivine has anomalously low contents of Ni, Co and Cr and high content of B inherited from sedimentary carbonate rocks, protoliths for MSSM. These features can be used to discriminate MSSM olivine from magmatic and mantle olivine.
2) Low-Ca olivine in MSSM may reflect crystallization from CO$_2$–rich fluid at relatively low temperature (<700 °C) at low aSiO$_2$. At higher temperature and/or lower f/CO$_2$ and higher aSiO$_2$, the olivine is expected to be replaced by monticellite via reaction with calcite and SiO$_2$ in fluid.

3) Strong correlation of the total amount of Li and Na with the content of P suggests a coupled incorporation of these elements in the MSSM olivine via heterovalent substitution at the octahedral and tetrahedral sites: $^\text{IV}\text{Si}^{4+} + ^\text{VI}(\text{Fe, Mg})^{2+} = ^\text{IV}\text{P}^{5+} + ^\text{VI}(\text{Li, Na})^+$. 

4) Correlation of REE+Y and Na contents suggests that REE+Y could be incorporated into the MSSM olivine structure via heterovalent substitution at the octahedral site: $2^\text{VI}(\text{Fe, Mg})^{2+} = ^\text{VI}\text{Na}^+ + ^\text{VI}(\text{Y, REE})^{3+}$. In contrast to high temperature magmatic systems, this mechanism maybe more important for olivine crystallizing at low temperature in low aSiO$_2$ environments such as in magnesian scarns.

Although our results provide a significant piece of information about the occurrence and composition of olivine in MSSM, we have to admit that the comprehensive understanding of the conditions of olivine crystallization in these rocks is currently missing. In particular, the conditions of crystallization of low-Ca olivine or monticellite in MSSM should be investigated in more details.

Besides MSSM, there is another class of rocks, where compositional variations of olivine were poorly characterized so far. These rocks are carbonatites, which could host olivine similar to that from MSSM by some parameters, for example, by extremely high Mg# approaching 100 (e.g. Guzmics et al., 2011). Although one can expect an elevated content of Ca in olivine from magmatic carbonatites (e.g. Di Stefano et al., 2018), there are reports of both relatively high (Guzmics et al., 2011) and very low Ca contents (Xie et al., 2019). The low Ca olivines from carbonatites are currently indistinguishable from olivine of MSSM origin. This could indicate a
similar metasomatic origin, or could be due to a lack of precise compositional data. Thus, further
systematic study of olivine from carbonatites is required to fill this gap in our knowledge.

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4).
References:


Rooney, T., Girard, G., Tappe S. (2020) The impact on mantle olivine resulting from carbonated silicate melt interaction. Contributions to Mineralogy and Petrology, 175, 56.


two nominally incompatible trace elements. Contributions to Mineralogy and Petrology, 174(10), 85.


Figure captions:

Fig. 1. Schematic map with marked sampling localities. Numbers (N), sample names and locations correspond to those in Table 1. The map is drawn using https://mapchart.net website.

Fig. 2. Comparison of EPMA and LA-ICP-MS data on the olivine composition from the same samples. Sample names correspond to those in Table 1 and on Figure 1. The error bars correspond to two standard deviations. Uncertainties of primary standards are not included, because they contribute insignificantly to the total uncertainty (Batanova et al., 2015, 2019). Linear regressions are calculated following the method of York et al. (2004), uncertainties of the regressions are calculated following Ludwig (1980).

Fig. 3. Petrographic features of studied MSSM samples. a – Ol-Cal-Sp association of the PB-15-3 sample in plane polarized (left) and crossed polarized (right) light; b – Ol-Cal-Phl association of the WS-15-4b sample in in plane polarized (left) and crossed polarized (right) light; c – back-scattering electrons image of Ol-Cal-Sp-Phl association of the 50363 sample with spots of LA-ICP-MS analyses; d – back-scattering electrons image of highly serpentinized olivine of the 74186 sample with spots of LA-ICP-MS analyses. Sp – spinel, Cal – calcite, Phl – phlogopite, Srp – serpentine, Mt – magnetite, Ilm – ilmenite.

Fig. 4. Minor elements (Mn, Ni, Al, Ca, Cr and Co) contents in studied skarn and silicate marble olivine samples (LA-ICP-MS data, Supplementary Table 2) in comparison with magmatic (De Hoog et al., 2010; Sobolev et al., 2007) and mantle olivine (De Hoog et al., 2010; Su et al., 2019). Sample names correspond to those in Table 1 and on Figure 1.

Fig. 5. P, Li and Na content in studied olivine samples (a, b) and comparison of Li + Na with P concentrations calculated as atoms per formula unit (apfu) (c). Sample names correspond to those in Table 1 and on Figure 1. Linear regression for the comparison of Li + Na with P (in apfu) is calculated following the method of York et al. (2004), uncertainties of the regression are calculated following Ludwig (1980).
Fig. 6. Dependence of measured Y, Dy, Yb and total REE contents in studied olivine samples from the content of Na. Sample names correspond to those in Table 1 and on Figure 1.

Fig. 7. Ti (a), B (b) and Zn (c) contents versus Mg# in studied olivine samples. Sample names correspond to those in Table 1 and on Figure 1. Ti and Zn contents in mantle olivine are from De Hoog et al. (2010) and Su et al. (2019), B – on the basis of Kent and Rossman (2002) and Chayka et al. (2020) data; Ti and Zn contents in magmatic olivine are shown for olivine from Baffin Island picrites (De Hoog et al., 2010), basalts from Canary Islands (Neumann et al., 1999), MORBs (Savelyev et al., 2018), arc basalts (Kamenetsky et al., 2018) and back-arc basalt (Nekrylov et al., 2018). B contents in magmatic olivine are shown only for kimberlites, lamproites and lamprophyres (Chayka et al., 2020; Nosova et al., 2017; Nosova et al., 2018) due to the lack of data on other magmatic suites.
<table>
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<th>Sample #</th>
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