

# Magma mingling at the Menominee pipe, USA? Contributions from texture and mineral chemistry

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## Introduction

Kimberlites and related rocks are petrographycally complex. They are hybrid rocks consisting of crystals derived from xenolith disaggregation and direct growth from the magma (Mitchell, 1986). There is a lack of knowledgement about the magmatic processes that occur before and during the emplacement. Furthermore, hydrothermal and supergene alterations during and post emplacement difficult the study of theses processes. An additional complication is the occurrence of magma mingling in kimberlites (Castillo-Oliver et al., 2016). This work presents a case of mineral sequence in a pipe from Hermansville, Menominee County (Michigan, USA) with the original composition partly preserved, thus allowing to discriminate among primary and secondary minerals.

## **Textural patterns**

The samples studied in this work belong to the hypabyssal facies. Ilmenite and phlogopite mega- and macrocrysts are set in a groundmass made up of olivine phenocrysts, carbonates, several ilmenite generations, spinel group minerals and djerfisherite.

Euhedral olivine phenocrysts are fresh and have complex zoning. The original rounded olivine core  $(ol_1)$  has a first euhedral olivine rim  $(ol_2)$  enriched in Fe. On its turn, this rim is overgrown by an outermost rim  $(ol_3)$  which has lower Fe contents. Fine-grained rounded sulphide inclusions (pentlandite, pyrrhotite) are common in the olivine core.

Two different types of unzoned spinel group minerals were identified in the groundmass. Spinel *sensu strictu* typically occurs as euhedral to anhedral crystals; although it is also found as inclusions in the outer part of the first rim of the olivine phenocrysts. This spinel is sometimes pseudomorphized by meixnerite ( $Mg_6Al_2(OH)_{18}$  4H<sub>2</sub>O). The second spinel-group mineral has compositions close to qandilite-magnetite fields and it is euhedral. However, it is also found as the last phase replacing Mgrich ilmenite macrocrysts.

Five textural types of ilmenite-group minerals are present in the Menominee pipe: 1) homogeneous macro- to microcrystic Mg-rich ilmenite, not replaced by other minerals; 2) macro- to microcryst Mg-rich ilmenite replaced along veinlets and grain borders by a sequence of rutile, geikielite and qandilite; 3) euhedral geikielite as very common inclusions in the outer part of the first olivine rim; 4) geikielite replacing Mg-rich ilmenite (type 4a), rutile microphenocryst (type 4b) and rutile included in olivine (type 4c); 5) Mg-rich ilmenite as inclusion in groundmass qandilite.

Rutile has 3 textural types: 1) euhedral rutile as very common inclusions in olivine, at the contact between the olivine core and it first rim, 2) rutile microphenocrysts (about 200  $\mu$ m) which are replaced by geikielite along their margins and fractures; 3) rutile replacing macro- to microcrysts of Mg-rich ilmenite. On its turn, this third type of rutile is replaced by geikielite and qandilite.

Groundmass carbonates are mainly calcite, which might be replaced by dolomite and barite. Djerfisherite ( $K_6$ (Fe,Cu,Ni)<sub>25</sub>S<sub>26</sub>Cl) occurs in the groundmass as anhedral grains up to 400  $\mu$ m in diameter. It is partly pseudomorphosed by a sequence of valleriite (2[(Fe,Cu)S]<sub>1.53</sub>[(Mg,Al)(OH)<sub>2</sub>]) and galena, followed by magnetite and cronstedtite ((Fe<sup>2+</sup>,Fe<sup>3+</sup>)<sub>3</sub>(Si,Fe<sup>3+</sup>)<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>).

#### **Mineral chemistry**

The composition of the rounded olivine core (ol<sub>1</sub>) is typically  $Fo_{90}$ , with ~0,4 wt % NiO; whereas the first euhedral rim (ol<sub>2</sub>) is both poorer in Fe and Ni (Fo<sub>89</sub> and ~0,2 wt.% NiO). The average composition of the outermost rim (ol<sub>3</sub>) is characterised by higher Fe contents, but lower Ni values (Fo<sub>91</sub> and ~ 0,1 wt.% NiO).

There are two different spinel-group minerals in the groundmass. The first is spinel *s.s.* (82-90% MgAl<sub>2</sub>O<sub>4</sub>, less than 0.08 Cr apfu) with average structural formula:  $[Mg_{0,84}Fe^{2+}_{0,17}][Al_{1,76}Fe^{3+}_{0,1}Cr_{0,08}Ti_{0,02}]O_4$ . The spinel s.s included in olivine phenocrysts has similar composition to the groundmass spinel s.s. The other spinel-group mineral has compositions of Cr-poor qandilite-ulvöspinel-magnetite series with significant contents of qandilite (29-55% Mg<sub>2</sub>TiO<sub>4</sub>, 20-46% Fe<sub>2</sub>O<sub>3</sub>, 5-19% MgAl<sub>2</sub>O<sub>4</sub>, 3-14% Fe<sub>2</sub>TiO<sub>4</sub>, less than 0.19 Cr apfu), corresponding with the next average structural formula:  $[Mg_{0,83}Fe^{2+}_{0,16}Mn_{0,01}][Fe^{3+}_{0,76}Ti_{0,43}Fe^{2+}_{0,42}Al_{0,34}Cr_{0,02}V_{0,01}]O_4$ . Both spinel s.s. and qandilite plot out of the kimberlite spinel fields established by Mitchell (1986) or Barnes and Roeder (2001). Qandilite is more enriched en Mg than the typical spinels from kimberlite fields, and those replacing ilmenite 4a and 4b are more enriched in Mg than those from the groundmass.

Type 1 and type 2 ilmenite have the same composition, with lower Mg (0,43-0,47 apfu Mg) content than other types of ilmenite as well as low Cr content  $(0,7-1,4 \text{ wt.}\% \text{ Cr}_2\text{O}_3)$ . Type 3 and type 4 ilmenite have very high Mg contents (0,5-0,8 apfu Mg), so they must be classified as geikielite. Type 3 ilmenite has 0,53-0,55 apfu Mg,  $1,9-3,0 \text{ wt.}\% \text{ Cr}_2\text{O}_3$ . Type 4a has 0,55-0,60 apfu Mg and  $0,8-1,2 \text{ wt.}\% \text{ Cr}_2\text{O}_3$ , while type 4b and 4c have higher contents of Mg (0,66-0,81 apfu) and Cr  $(1,6-5,7 \text{ wt.}\% \text{ Cr}_2\text{O}_3)$ . Compositions of type 5 ilmenite are similar to those of type 4b and type 4c ilmenite.

The three types of rutile have similar composition, they have 0,9-2,0 wt.% Nb<sub>2</sub>O<sub>5</sub>, 0,8-4,5 wt.% Cr<sub>2</sub>O<sub>3</sub> and 0,6-0,9 wt.% V<sub>2</sub>O<sub>3</sub>.

Djerfisherite has the next average structural formula:  $[K_{5,86}Na_{0,03}Ca_{0,03}]$   $[Fe_{17,46}Ni_{6,64}Cu_{0,80}Co_{0,15}]$   $S_{26}Cl_{1,00}$ . This djerfisherite is Ni-rich (5,5-7,9 apfu Ni) and Cu-poor (0,4-1,2 apfu Cu).

#### **Discussion and conclusions**

Zoning in the olivine phenocrysts is interpreted as the result of an epitaxial overgrowth of corroded mantle xenocrysts (ol1), developed under non-equilibrium conditions. Rutile co-crystallized with the early stages of the first forsterite rim, whereas geikielite and spinel s.s. started to crystallize during the late stages of this rim. The last olivine overgrowth (ol<sub>3</sub>) would co-crystallize with qandilite.

Rutile in kimberlitic rocks is commonly interpreted as a xenocryst resulting from disaggregation of a wide variety of rocks, which may have either a crustal or a mantle origin (eclogites, MARID, pyroxenites, metasomatized peridotites). However, it has also been found as diamond inclusions and or as intergrowths with diamond (Meinhold, 2010). Its composition has been used to constrain its source rock. Like this, while Cr-poor rutile could be derived from both crustal and off-cratonic or cratonic mantle rocks; Cr-rich rutile (>1,7 wt.% Cr2O3) is thought to be exclusively related to the cratonic mantle (Malkovets et al., 2016). However, the rutile crystals found as inclusions in olivine or disseminated in the groundmass of the Menominee pipe cannot be xenocrysts. Instead they formed during the early stages of magma crystallization, immediately followed by geikielite and spinel s.s., well before the crystallization of the first olivine rim.

Occurrence of two different spinels (spinel s.s. and qandilite-rich spinels) in the same groundmass can be interpreted as an evidence of magma mingling. Despite both spinels are not exactly contemporaneous, both were formed during groundmass crystallization. Both spinels are unzoned, and therefore they do not follow any of the typical kimberlitic trends. The early crystallization of aluminian spinels has been explained as a result of the cessation of the phlogopite crystallization (Pasteris, 1983), but in this case the development of spinel could be favoured by an increase in the fO<sub>2</sub>. The occurrence of qandilite-rich spinels in the last stages of crystallization could suggest the existence of a very evolved kimberlitic magma, as those mentioned in the Jos and Benfontein kimberlites (Mitchell, 1986).

Finally, djerfisherite is a Cl-bearing potassium sulfide found in meteorites, alkaline ultramafic rocks and carbonatites. Sharygin et al. (2007) suggest a late magmatic origin of djerfisherite in the Udachnaya-East kimberlite groundmass, formed at shallow depths and at  $T \le 800^{\circ}$ C. Djerfisherite was found also in mantle xenoliths as interstitial rims around Fe–Ni–Cu sulfides and around sulfide globules (Sharygin et al., 2007) and as xenocrysts/megacrysts around primary sulfide globules and as daughter phase in melt inclusions (Kamenetsky et al., 2009). Djerfisherite was also found as inclusions in diamonds (Zedgenizov et al., 1998). However, the experimental data indicated that djerfisherite is not stable at pressure greater than 3Gpa (Minin et al., 2015). Therefore, djerfisherite included in diamond and mantle xenoliths formed by interaction between xenoliths and kimberlitic melts, and the presence of djerfisherite can be an indicator of Cl enrichment of kimberlite melt (Sharygin et al., 2007; Minin et al., 2015). The common occurrence of djerfisherite at the Menominee pipe indicates a high activity of volatiles (S and Cl) and alkalis during melt crystallization, and could be favoured by the fractionation of K to the melt instead of being used to crystallize phlogopite.

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### References

- Castillo-Oliver M, Galí S, Melgarejo JC, Griffin WL, Belousova E, Pearson NJ, Watangua M, O'Reilly SY (2016) Trace-element geochemistry and U–Pb dating of perovskite in kimberlites of the Lunda Norte province (NE Angola): petrogenetic and tectonic implications. Chem. Geol. 426: 118–134
- Barnes SJ, Roeder PL (2001). The range of spinel compositions in terrestrial mafic and ultramafic rocks. J. Petrol. 42: 2279–2302
- Kamenetsky VS, Maas R, Kamenetsky MB, Paton C, Phillips D, Golovin AV, Gornova MA (2009) Chlorine from the mantle: Magmatic halides in the Udachnaya-East kimberlite, Siberia. Earth Planet. Sci. Lett. 285: 96–104
- Malkovets VG, Rezvukhin DI, Belousova EA, Griffin WL, Sharygin IS, Tretiakova IG, Gibsher AA, O'Reilly SY, Kuzmin DV, Litasov KD, Logvinova AM, Pokhilenko NP, Sobolev NV (2016) Crrich rutile: A powerful tool for diamond exploration. Lithos 265: 304-311
- Meinhold G (2010) Rutile and its applications in earth sciences. Earth-Science Reviews 102: 1-28
- Minin DA, Sharygin IS, Litasov KD, Sharygin VV, Shatskiy A, Ohtani E (2015) High-pressure stability of djerfisherite: Implication for its origin in diamonds and mantle xenoliths. Advances in high Pressure Research II: Deepest Understanding 2015: 14
- Mitchell (1986) Kimberlites: mineralogy. geochemistry and geology. Plenum Press, New York. 442pp.
- Pasteris, J.D. (1983): Spinel zonation in the De Beers kimberlite, South Africa: possible role of phlogopite. Can. Mineral. 21: 41-58
- Sharygin VV, Golovin AV, Pokhilenko NP, Kamenetsky VS (2007) Djerfisherite in the Udachnaya-East pipe kimberlites (Sakha-Yakutia, Russia): paragenesis, composition and origin. Eur. J. Mineral. 19: 51–63
- Zedgenizov DA, Logvinova AM, Shatskii VS, Sobolev NV (1998) Inclusions in microdiamonds from some kimberlite diatremes of Yakutia. Dokl. Akad. Nauk 359: 204–208