Exsolution *vs*. non-exsolution microstructures : geological implications

MARIA DOLORES RUIZ-CRUZ (1*), ENCARNACION PUGA (2)

(1) Facultad de Ciencias. Campus de Teatinos. Universidad de Málaga. 29071 Málaga (España)
(2) Instituto Andaluz de Ciencias de la Tierra. Avda. de las Palmeras, 4. CSIC-Universidad de Granada. 18100 Armilla (España)

INTRODUCCIÓN

The term "exsolution" is generally restricted to the formation, on cooling, of two separated phases from one homogeneous solid solution. Nevertheless, some uncertainty exists regarding the processes that produce determined intergrowths during decompression of rocks submitted to high- or ultrahigh pressure (HP or UHP) conditions. However, it is a challenging scientific topic to distinguish the exsolution from the non-exsolution microstructures and decipher their geological implications.

Liou et al. (2009) emphasize that distinction of exsolution microstructures from primary inclusions must be based on their geometric topotaxy and chemistry. In this paper, we report some representative examples of exsolution microstructures at the same time that some new criteria for their identification are proposed. Some of these examples have been already published whereas some others are presented here for the first time.

Exsolution microstructures in olivine

Ruiz Cruz et al. (1999) described the presence of Ti-Fe-Cr oxides in spinifex-like textured olivine from secondary harzburgites of the Mulhacén Complex (Betic Cordillera). Chromite and ilmenite particles form parallel, chromite-rich and ilmenite-rich bands, extending along the *a*-axis of the host olivine and displaying a fixed orientation relationship with olivine, indicating that both phases formed during a common exsolution process. Chromite particles commonly are accompanied by lamellae of talc and/or enstatite, both showing a consistent orientation relationship with olivine (Fig. 1). Talc formation may be explained by exsolution, together with spinel, from olivine containing OH-groups, probably related to incomplete dehydration of serpentine during olivine formation. Ti-Fe oxides exsolution in olivine have been previously described and interpreted as formed during decompression of UHP peridotites. We concluded that exsolution of chromite+silicate and ilmenite occurred during the retrograde stage that followed the climax of the eo-Alpine metamorphic event, with estimated P-T conditions of 650-750ºC and 16-25 kbar.

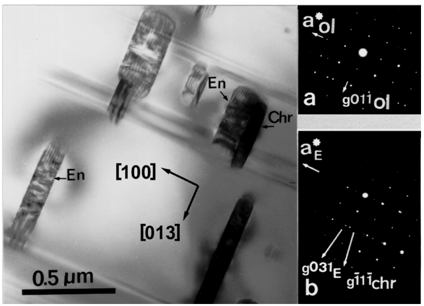

Fig. 1. TEM images of Chromite (Chr)-enstatite (En) and enstatite particles. The h31* *rows of clinoestatite coincide with the* hkk* *rows of olivine (Ol). (In the SAED patterns, E = Enstatite).*

Exsolution microstructures in garnet

We present several examples of oriented inclusions in garnet, most of them interpreted as exsolutions formed during decompression of the UHP event that affected the deepest formations of the Alpujárride complex (Betic-Rif Cordillera) (Ruiz Cruz and Sanz de Galdeano, 2013).

- Rutile exsolution

Densely packed rutile needles and rods appear frequently as composite inclusions made of rutile and a silicate phase (Fig. 2) identified as pyroxene by Raman. The orientation relationships is $\{001\}_{Rt}//\ \{110\}_{Grt}$. The proposed substitution mechanisms are the coupled substitutions $Na^+ + Ti^{4+} = Ca^{2+} + Al^{3+}$ and $M^{2+} + Ti^{4+} = 2Al^{3+}$.

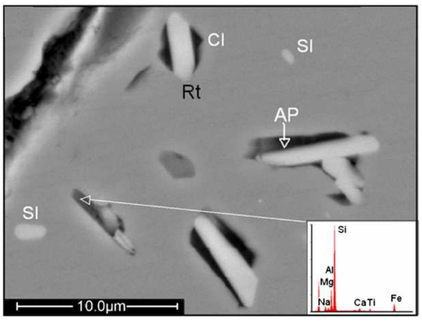

Fig. 2. BSE image showing single (SI) and composite (CI) rutile+pyroxene inclusions.

- Quartz+coesite exsolution

Pseudo-cubic or prismatic silica (quartz and coesite) inclusions in garnet appear aligned (Fig. 3). The inclusions are surrounded by anomalous birefringent fields indicating strong strain of garnet and by small microfractures (Fig. 3, inset). The orientation analysis indicated that $\{0001\}_{Qz}//\ \{001\}_{Coe}//\ \{110\}_{Grt}$.

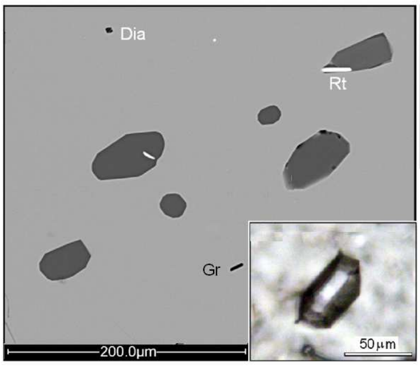

Fig.3. BSE image showing size and orientation of the quartz+coesite±rutile inclusions. Inset: Morphology of quartz and small cracks in garnet. Dia: diamond. Rt: Rutile. Gr: Graphite.

Estimation of the initial composition leads to a notable increase of the Si content in garnet, which is coupled with both loss of Fe^{3+} and vacancies in VI and VIII.

palabras clave: Metamorfismo de alta y ultra alta presión; microestructuras de exolución

key words: High- and ultra-high pressure metamorphism, exsolution microstructures

* corresponding author: mdruiz@uma.es

- Apatite exsolution

Some garnet cores show high density of apatite inclusions, which are seen as prisms, rods, needles and as rarer hexagonal crystals.

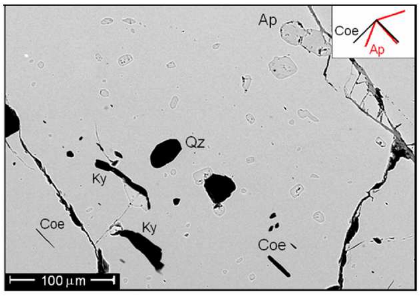

Fig.4. BSE image showing size and orientation apatite (Ap), quartz (Qz) and coesite (Coe). Inset: Elongation directions of coesite needles (black lines) and apatite prisms (red lines).

Apatite coexists with quartz, kyanite and needles of coesite (Fig. 4). Apatite needles and prisms define equilateral triangles, whereas coesite needles show an orthogonal pattern. Apatite shows {0001} parallel to the three equivalent [100] directions of garnet, whereas the orientation of coesite is controlled by the [110] directions. Apatite is interpreted as result of exsolution of P + F-rich garnet. Phosphorus can enter the garnet structure through the coupled substitution of $P^{5+} + Na^{+} \rightarrow Si^{4+} + Ca^{2+}$. In the current composition of our apatite-bearing garnet, the slight excess of Si and Al are compensated by the presence of vacancies in the octahedral positions.

- Kyanite exsolution

Some studied garnets contain very abundant small prismatic and needle-shaped kyanite inclusions. Kyanite shows {3-20} coincident with the three equivalent [100] directions of garnet. Estimation of the initial composition of garnet indicates an excess of Al, which can be interpreted in crystallochemical terms, as due to solid solution of garnet and aluminosilicate.

- Graphite exsolution?

High density of variably sized graphite inclusions have been identified in some garnets (Fig. 6) (Ruiz Cruz, 2013).

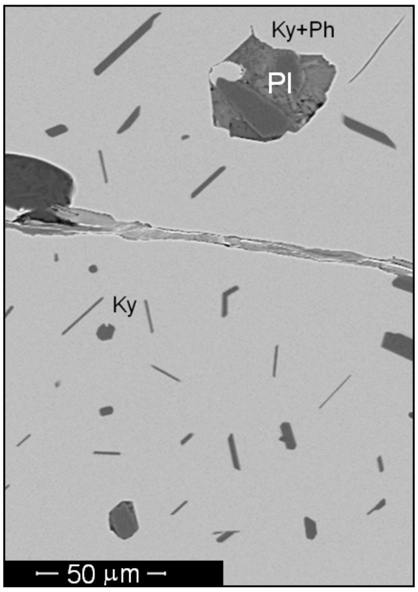

Fig.5. BSE image showing a zone rich in prismatic kyanite (Ky) and composite kyanite+ phengite primary inclusions (Pl).

The SAED patterns indicate that $c_{Gr}//\{111\}_{Grt}$ and $\{1011\}_{Gr}//\{110\}_{Grt}$. These topotactic relationships suggest that carbon precipitated from an originally homogeneous solid solution of carbon in garnet, through direct substitution of C^{4+} for Si^{4+}.

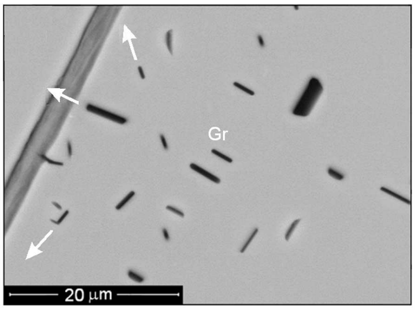

Fig.6. BSE image showing the graphite (Gr) density and the preferred orientations.

Exsolution microstructures in apatite?

We have studied mono- and by-phased fluid inclusions (FI) in apatite. FI are elongated with uniform size (~1x10 μm) oriented either in parallel to the c axis of apatite or following three symmetrically related directions perpendicular to c of apatite (Fig. 7). The EDX spectra show variable amounts of C, Cl, Na and K, indicating the presence of a C-bearing vapour phase and saline brines. There are two possible explanations for the origin of these fluid inclusions: 1) A primary origin linked to the prograde apatite crystallization; and 2) That the fluid inclusions exsolved from C- and Na+K-rich apatite during exhumation.

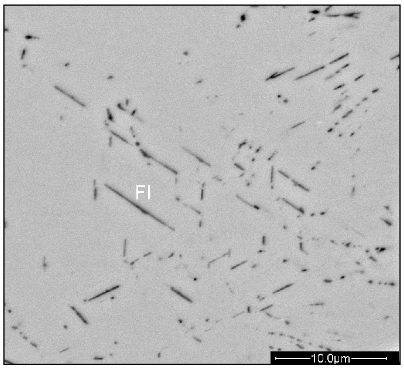

Fig.7. BSE image showing the size and the geometrical distribution of the fluid inclusions (FI) in apatite.

Conclusions

The examples presented comply with the common diagnostic features proposed by Liou et al. (2009) for identification of exsolution microstructures. In addition we can add that composite oriented inclusions can be unambiguously interpreted as exsolution microstructures. Our results indicate that, in absence of well-preserved HP- or UHP phases (e.g. coesite, diamond, jadeite), identification of exsolution microstructures can be key in recognition of HP and UHP metamorphism and thus in defining the subduction depth.

ACKOWLEDGEMENTS

This study has received financial support from the Project CGL 2012-31872 (Ministerio de Economía y Competitividad, Spain).

REFERENCES

*Liu, L., Yang, J. X., Zhang, J. F., et al. (2009): Exsolution microstructures in ultrahigh-pressure rocks: Progress, controversies and challenges. Chinese Sci Bull, 2009, **54**, 1983-1995.*

*Ruiz Cruz, M.D. (2013): Are nanotubes and carbon nanostructures the precursors of coexisting graphite and micro-diamonds in UHP rocks? Diamond Relat. Mater. **40**, 24-31.*

*Ruiz Cruz, M.D., Puga, E., Nieto, J.M. (1999): Silicate and oxide exsolution in pseudo-spinifex olivine from metaultramafic rocks of the Betic Ophiolitic Association: A TEM study. Am. Mineral., **84**, 1915-1924.*

*Ruiz Cruz, M.D., Sanz de Galdeano, C. (2013): Coesite and diamond inclusions, exsolution microstructures and chemical patterns in ultrahigh pressure garnet from Ceuta (Northern Rif, Spain): Lithos, **177**, 184–206.*