Dating high-grade south European Variscan evolution: constraints from trace element chemistries of garnet, zircon and orthopyroxene on U-Pb zircon ages.

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1. TOPIC

In order to provide finer constraints on the geochronology of the Variscan metamorphism, U-Pb spot ages and trace element analyses on zircon (LA-ICP-MS, IGG-CNR, Pavia) coupled with major and trace element analyses on garnet and orthopyroxene (SEM, Geomineralogico Dep., Bari University) were performed *in situ* on a thin section of a granulite facies rock of Serre Massif (Calabria, Southern Italy).

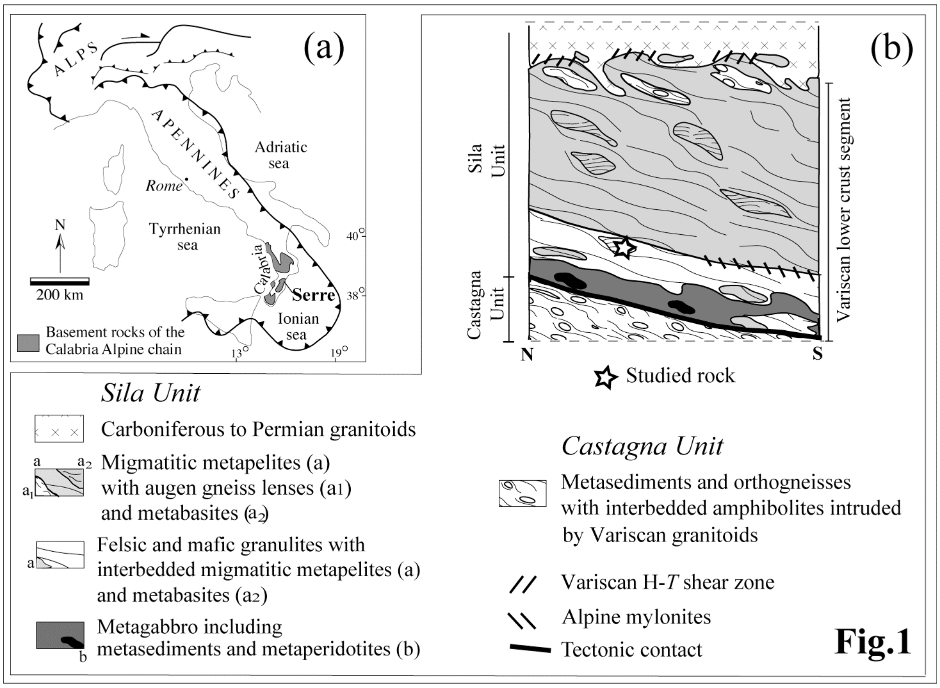
The trace element partition within zircon-garnet-orthopyroxene allows a better understanding of:

1) P-T-t paths during high grade metamorphism;
2) the tectonic evolution of a fragment of Southern European Variscides.

2. GEOLOGICAL CONTEXT AND PETROGRAPHY

The studied garnet-bearing metabasic rock occurs within the felsic granulites of the lower portion of the Variscan deep crust section of the Serre Massif (**Fig.1**) which includes rocks derived from pre-Cambrian magmatic protoliths (Micheletti et al., 2008) and deeply reworked by Variscan metamorphism. They bear memory of: 1) prograde stage from amphibolite to granulite facies metamorphism and 2) multistage dehydration and decompression during the Variscan evolution under changing P-T from 1.03 GPa and 900°C to 0.7 GPa and 700°C (Acquafredda et al., 2008).

The studied rock consists of plagioclase, garnet, biotite, orthopyroxene, quartz, K-feldspar and, as accessory phases, zircon, apatite and opaque minerals. A porphyroblastic garnet covers more than 50% of the thin section (**Fig.2**), straddling two layers with different abundance of biotite and orthopyroxene. Garnet includes biotite, plagioclase and apatite in the core, and apatite, plagioclase and one zircon grain in the rim. The porphyroblast is rimmed by a symplectitic corona consisting of Opx+Pl+Bt+opaques+Zrn+Ap and its edge shows profound engulfments (**Fig.2**) indicative of participation of garnet rim to the formation of corona. Few grains of garnet occur also within the symplectitic corona.

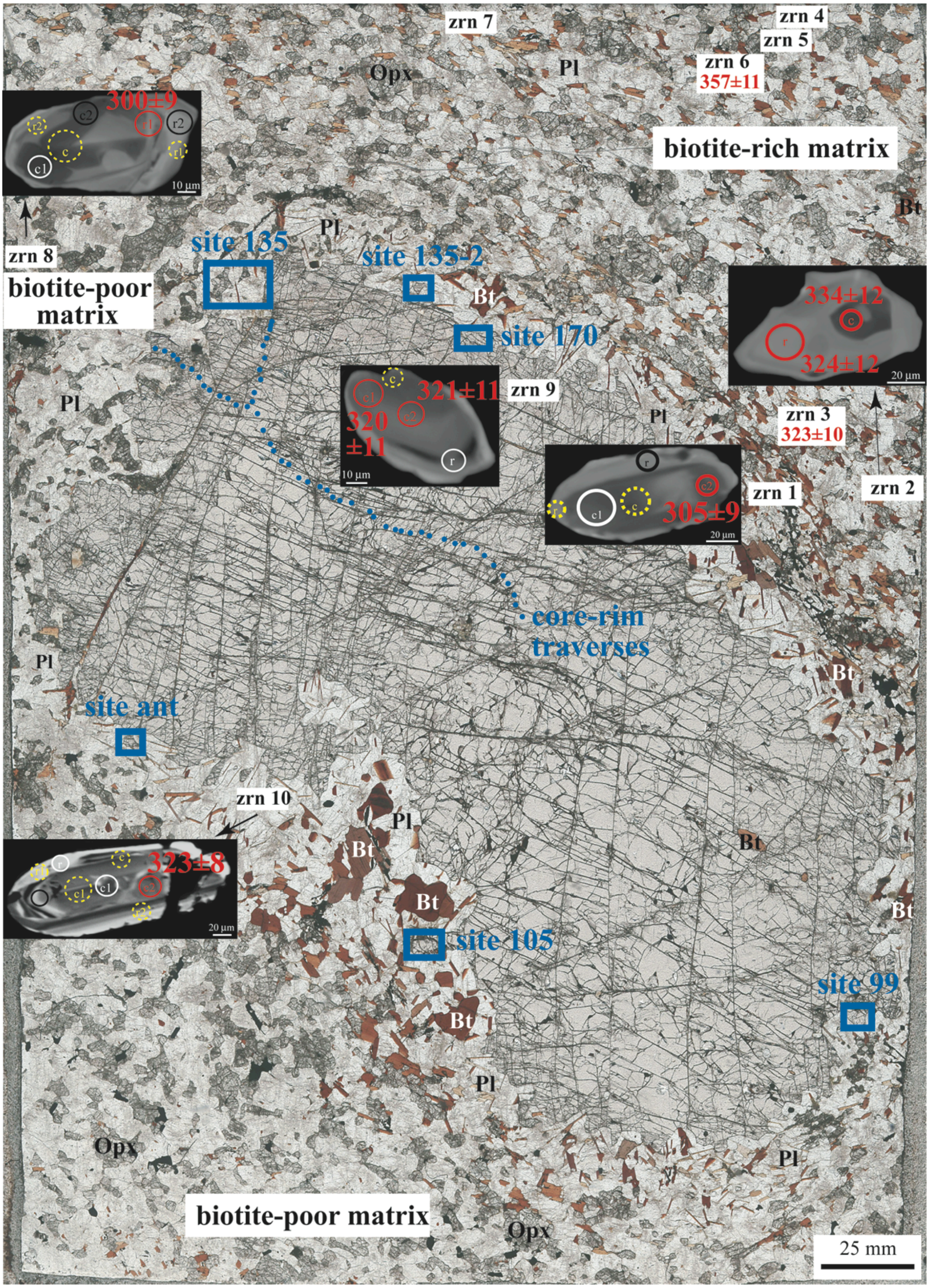


3. ZIRCON TEXTURES AND U-Pb RESULTS

Ten zircon grains (250-50 μm in dimensions) were identified in the thin section: eight in the Bt-rich matrix, one within the corona and one in the rim of the porphyroblastic garnet (**Fig.2**). Zircon grains show generally core-rim structures and cores are often "invaded" by homogeneous lobate rims likely indicative of dissolution and re-growth, related to interaction with fluids and/or melts (e.g. Corfu et al., 2003; Geisler et al., 2007). Some zircon cores show chaotic textures probably induced by the high-grade metamorphism (Rubatto and Gebauer, 2000).

All zircon grains have been dated in situ producing 9 concordant ages ranging from 357±11 to 300±9 Ma **(Fig.2)**. The core domains of zircons in the matrix give the oldest concordant ages (357±11 Ma-334±12 Ma); the other core domains from different textural sites give an age group ranging from 324±12 to 320±11 Ma (5 concordant data) with a mean concordia age of **323±2 Ma** (MSWD=0.002). Younger concordant ages of 305±9 Ma (zrn 1) and 300±9 Ma (zrn 8) are relative to low luminescent inner rim invading cores of zircon in matrix. Three luminescent rim domains giving apparent ages from 305 Ma to 296 Ma having low probability of concordance were determinated on grains from matrix, symplectitic corona and rim of garnet.

Fig.2



zrn 7
zrn 4
zrn 5
zrn 6
357±11
Opx
Pl
300±9
c2
r1
r2
r2
c
r1
c1
10 µm
biotite-rich matrix
Bt
zrn 8
biotite-poor
matrix
site 135
Pl
site 135-2
Bt
site 170
334±12
c
r
324±12
20 µm
Pl
c
c1
321±11
zrn 9
320
±11
c2
r
10 µm
Pl
zrn 3
323±10
zrn 2
r
c2
zrn 1
r
c1
c
305±9
20 µm
core-rim
traverses
Pl
Bt
site ant
zrn 10
Pl
r1
r
c
323±8
c1
c1
c2
r2
20 µm
Bt
Bt
Bt
Bt
site 105
Bt
site 99
Bt
Pl
Opx
Pl
biotite-poor matrix
Opx
25 mm

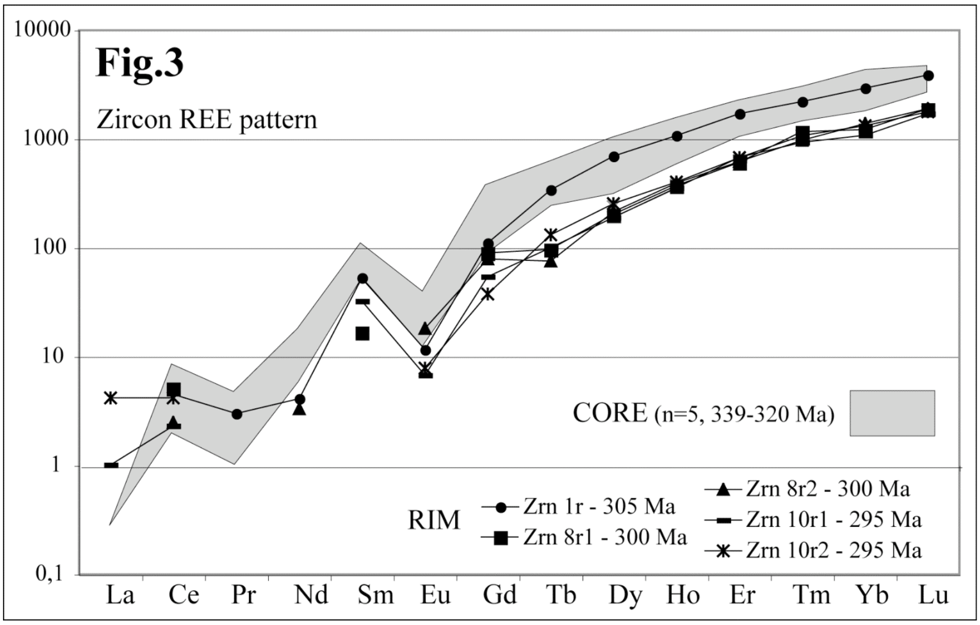
4. CHEMISTRY

4a. Zircon chemistry

Ten micro-domains were investigated from four zircon crystals (grains 1, 2, 9 and 10; **Fig.2)**. Core and rim show variable trace element contents: Th (564-97ppm), U (1110-324ppm), Pb (15-4ppm), Hf (10164-18219 ppm), Y (2477-637), Nb (7-2ppm), Sc (390-587 ppm), Ti (7-98 ppm) and Ta (0.6-4.4 ppm). Y, Nb, Th, U and Pb contents tend to be higher in the core regions and U is more depleted than Th in the overgrowths. The analysed domains have moderate to high Th/U ratio (0.15-0.57).

The crystal 10 in corona is peculiar since its core shows the highest contents in Pb (15 ppm), Th (564 ppm), U (1110 ppm), Y (2477 ppm), HREE (∑HREE=1731 ppm), the highest Th/U ratio (0.51) and a positive anomaly of Ce.

The REE abundances in the analysed zircons vary from 439 ppm to 1764 ppm and their distribution defines a steep pattern with low LREE and high HREE contents having Yb_N/Ce_N ratio ranging from 629 to 447 (means in cores and rims, respectively) (**Fig.3**). In details it appears that: (i) four out of five analysed rims have lower contents of MREE-HREE than the cores, (ii) core regions show steeper LREE than rims and negative Eu anomalies, and (iii) when core and outer core have been analysed (crx 10) the latter appears poorer in REE.



4b. Garnet chemistry

Garnet is almandine (48.5-53.3)-pyrope (34.1-28.4)-grossular (11.4-8.9) solid solution with minor andradite (3.9-4.6) and spessartine (1.8-2.9) components. It shows increase in almandine, spessartine and andradite and decrease in pyrope and grossular towards the rim. The Mg-number ($Mg/(Mg+Fe^{2+}) \times 100$) decreases from 41.3 to 27.3 reaching the lowest value in the site 135 (rim) and in the fragments of garnet in the symplectitic corona (**Fig.2**).

To detail the trace element variation, garnet has been analysed along two crosscutting core-rim traverses (**Fig.2**). Four sites along the present rim (135, 170, 99 and 105) and three fragments of garnet grains in the symplectitic corona were also analysed (**Fig.2**).

The trace-element distribution shows an important increase of Cr, V, Y and Sc towards the rim and the highest enrichment occurs in the site 135 (**Fig.2**). The MREE and HREE are very abundant and togheter with Y decrease in the outer core and increase towards the rim reaching the highest contents in the site 135 (**Fig.4**).

The HREE profiles (Gd-Lu) are different in the three regions of garnet (**Fig.5**): (1) in the *inner core* the HREE profile is nearly flat to moderately fractionated with ∑HREE=2463 ppm, (2) in the *outer core* region HREE decrease (∑HREE=1434 ppm), and (3) in the *rim* regions the HREE are variable from 2015 ppm to 14784 ppm (as in the site 135; **Fig.2**).

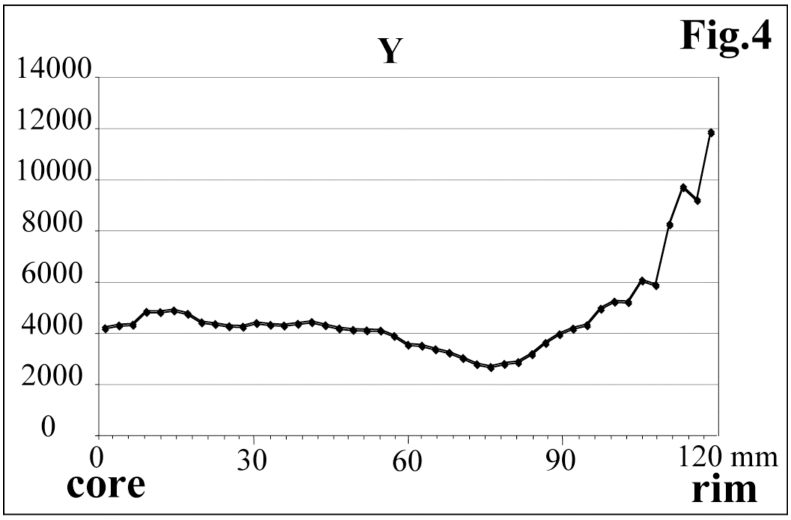
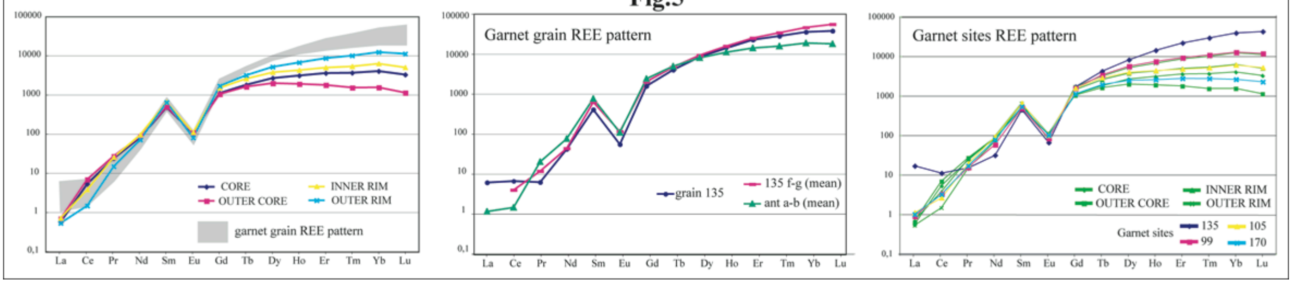


Fig.4

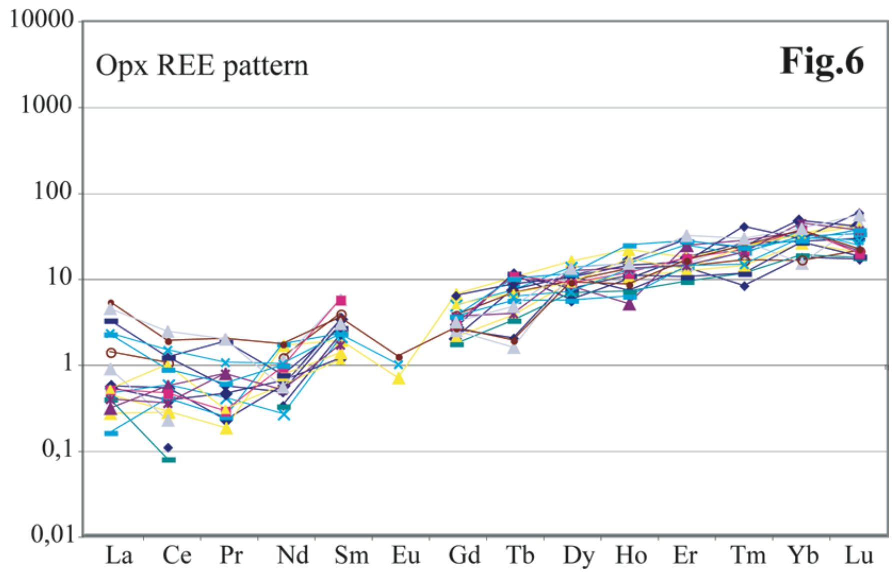
Fig.5



4c. Orthopyroxene chemistry

Orthopyroxene contains 1.0-3.3 wt% of Al_2O_3 and its Mg-number ($Mg/(Mg+Fe^{2+})$ x 100) varies from 64.0 to 68.5 in biotite-rich, biotite-poor matrix and in proximity of symplectitic corona around garnet. There is not significant chemical difference between core and rim both in matrix and corona. The contents of Cr, V and Zn in orthopyroxene depends on the textural sites. Orthopyroxene from the biotite-poor matrix is richer in these elements than that from the biotite-rich matrix (Cr=353-575 ppm versus 300-350 ppm; V=274-387 ppm versus 220-275 ppm; Zn=453-528 versus 420-480 ppm). The highest abundances of the above elements have been determined in the orthopyroxene from corona near the 135 site (**Fig.2**), where even the Sc content is higher (103-154 ppm, n=5).

HREE do not show systematic variations (∑HREE from 5.0 to 17.4, n=30). Generally, they show fractionated patterns (Yb_N/Gd_N=12.42, n=30, **Fig.6**).



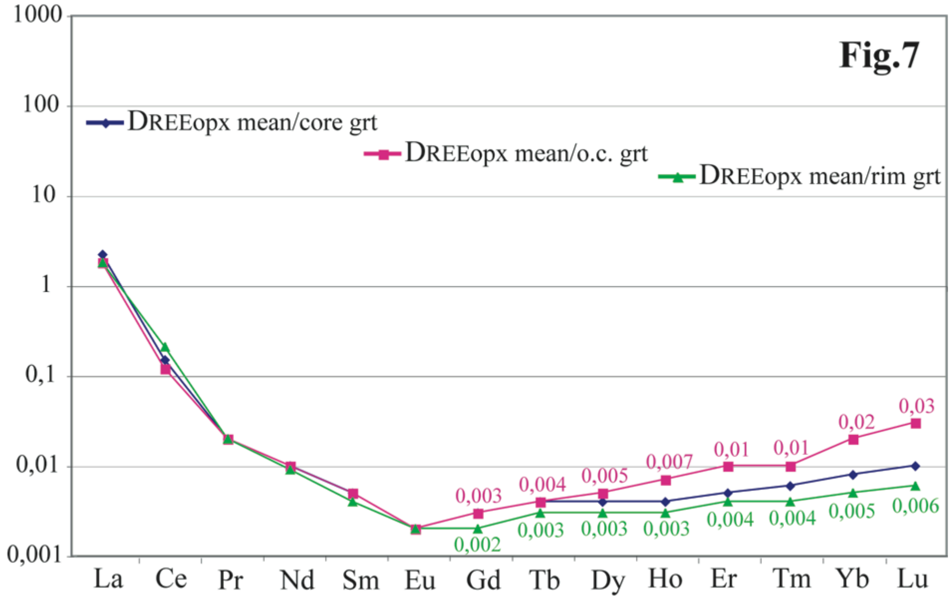
5. REE DISTRIBUTION BETWEEN ZIRCON, GARNET AND ORTHOPYROXENE

The geological significance of the U-Pb ages might be derived from the textural relationships between zircon, orthopyroxene and garnet which are competitors at various degree for HREE. Therefore, when coexisting, they will influence each others compositions.

Accordingly, apparent distribution coefficients for REE contents (D_{REE}) were calculated in the pairs orthopyroxene-garnet and zircon-garnet in specific domains and compared with the empirical D_{REE} values inferred to represent metamorphic equilibrium in granulite and eclogite facies rock-types (Rubatto, 2002; Whitehouse and Platt, 2003; Buick et al., 2006; Harley and Kelly, 2007 and reference therein; Orejana et al., 2010), as well as, with the experimental results under different temperatures (Rubatto and Hermann, 2007).

5a. Orthopyroxene-garnet relationship

The $D_{REEopx/grt}$ calculated between orthopyroxene (from matrix and corona) and garnet (core, outer core and rim enriched in HREE) for our rock are represented in **Fig.7**. The calculated $D_{REEopx/grt}$ show: (i) a decrease from La to Gd, (ii) an increase progressively from Gd to Lu, and (iii) a fall in the range suggestive of equilibrium from Er to Lu in the combination orthopyroxene and outer-core of garnet, and (iv) are far from the equilibrium for the combination of orthopyroxene from corona with garnet rim or- with garnet grains from corona.



5b. Zircon-garnet relationship

D_{HREE} calculated between zircon domains and different regions of porphyroblastic garnet are represented in **Fig.8**. The D_{HREE} values show: (1) a progressive increase from D_{Gd} to D_{Lu} depicting positive trends controlled by increase of substitution of small cations for Zr (Schaltegger, 2003) and (2) mostly parallel trends for all combinations evidencing variable partitioning. The combination of core-core regions give $D_{REEzrn/grt}$>1 only for Lu; the trends relative to combinations with the outer core of garnet reach values >1 from Er to Lu if zircon cores are considered (**Fig.8**); the rim-rim combinations give $D_{REEzrc/grt}$ values < 1. If we look at the apparent ages of the zircon domains and their location, it appears that: (i) core regions dated from 320±11 Ma to 325±11 Ma in matrix, in rim of garnet and in corona together with rim dated 305±9 Ma in matrix combined with outer core region of garnet display the highest distribution coefficients (**Fig. 8b**), (ii) core regions dated 339±11 and 336±10 Ma combined with outer core region of garnet show lower D_{HREE} (**Fig.8b**) and (iii) the rims dated 300 to 296 Ma give even lower D_{HREE}.

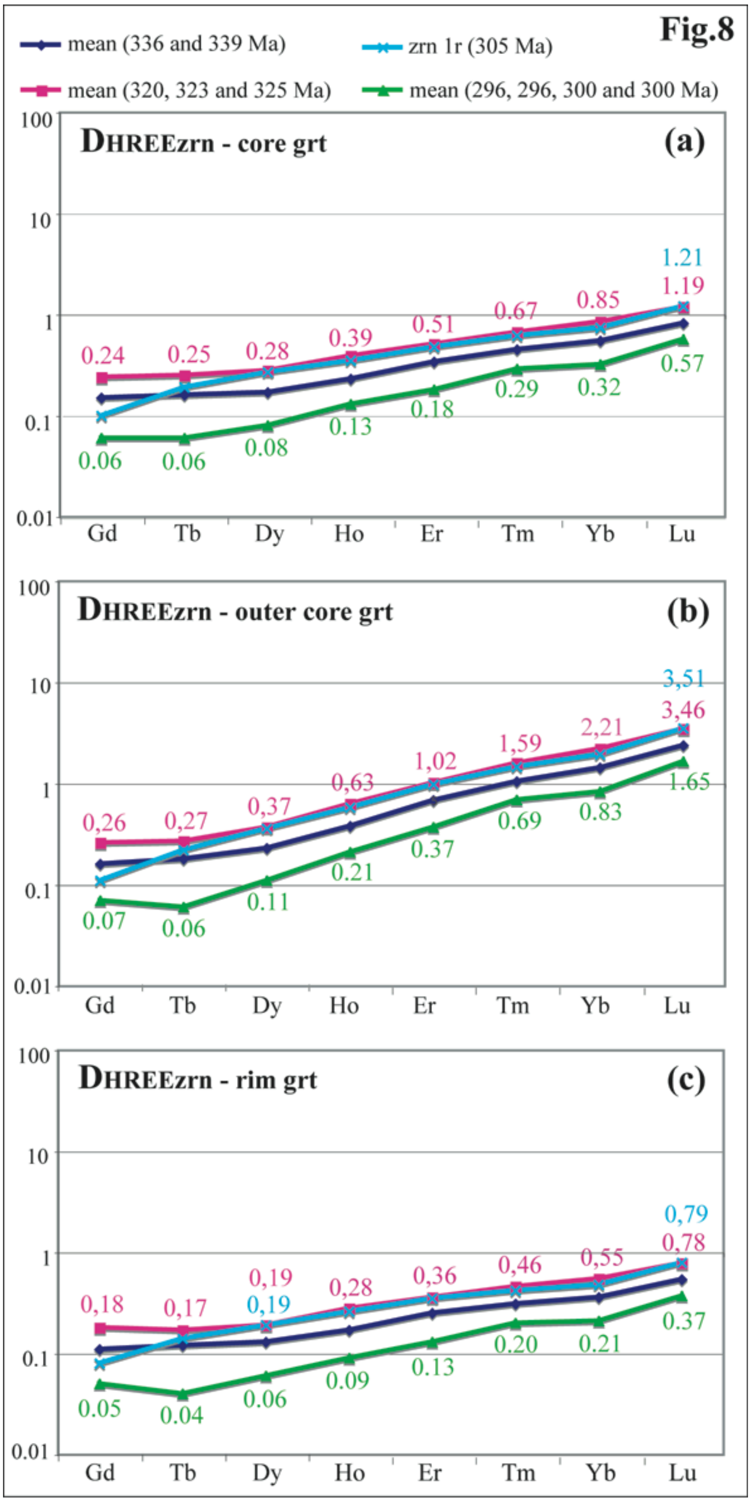
Our data however arrange along positive and linear trends as happens for some natural and experimental examples (**Fig.9**). The decidedly lower D_{HREE} values calculated for this example relatively to empirical and experimental results, is a consequence of the significantly higher contents of HREE in the garnet than in zircon.

6. DISCUSSION

In order to gain information relative to the geological significance of the U-Pb age data on zircon it would be better to keep in mind the following points:

- The quite similar chondritic REE patterns for core and rim regions of garnet from La to Dy and the abundances of MREE and HREE as well as the similarities of the differentiated patterns of zircon (both core and rim) from different structural sites, seem to indicate growth in an *open system*. This environment would prevent compositional change in the accessory zircon due to crystallization of garnet.
- Garnet regions of the present example are many times richer of REE than the competitor zircon and orthopyroxene. Only the outer core of garnet shows slightly lower contents from Er to Lu than zircon cores.
- The quite different chemistry between core and rim of zircon likely indicates episodes of new growth more than modification (Rubatto 2002).
- On the basis of calculated $D_{HREEopx/grt}$ for different domains of garnet emerge that the orthopyroxene appears approaching equilibrium with core and outer core regions but not with rim regions of garnet (**Fig.7**). This fact, together with the strong increase of HREE towards the garnet rim imply that garnet rim formed earlier than corona and, probably, orthopyroxene from corona is a remain of the matrix. The enrichement of HREE in the present rim of garnet might reflect retention during the breakdown or, alternatively, re-opening of the system with input of HREE.
- The positive, linear and parallel trends described by $D_{REEzrn/grt}$ are expression of:

a regolar rule of the partitioning of the HREE. On this basis, the calculated $D_{REEzrn/grt}$ values seem to be indicative of steps of approaching equilibrium under different physical conditions.



A comparison with the literature data occurs (**Fig.9**):

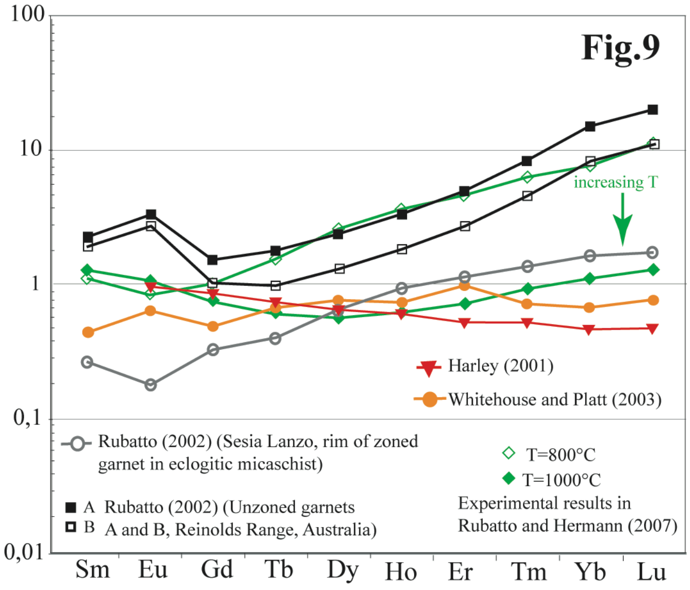
- according to Harley (2001) and Withehouse and Platt (2003) a negative or flat trends with $D_{REEzrn/grt}$ values ≤ 1 are indicative of equilibrium between zircon and garnet in granulites.
- Rubatto (2002) suggests in natural examples positive and linear trends with $D_{REEzrn/grt}$ values increasing from Gd (~1) to Lu (~10). A sample of eclogite from Sesia Lanzo Zone shows a

garnet rim considered in equilibrium with zircon having a trend of $D_{REEzrn/grt}$ values quite similar to the our example. However, it has to be noticed that garnet of the eclogite sample grew under increasing P.

-The experimental results of Rubatto and Hermann (2007) evidenced linear and positive trends with $D_{REEzrn/grt}$ values >1 for HREE. In addition these Authors show that $D_{REEzrn/grt}$ values decrease when the T-equilibrium increase in the range 800-1000°C.

The patterns and $D_{REEzrn/grt}$ values derived from literature indicating equilibrium are different; the natural examples (Harley, 2001; Rubatto, 2002; Whitehouse and Platt, 2003; Buick et al., 2006) and the experimental results (Rubatto and Hermann, 2007) refer to different reservoirs, different compositions of garnet, homogeneous or zoned garnet, different P/T conditions (from ~40°Ckbar^{-1} to more than 100°C kbar^{-1}), open and closed systems. So some caution over precise quantitative application should be used until the dependance of the distribution coefficients on the above facts has been evaluated. In addition, the duration of the high T metamorphic stages might have a bearing since long lived H-T conditions might influence elemental diffusion. In fact, in the case study, the core-rim decrease of Mg-number and increase of spessartine indicate decrease of T and P during garnet growth in line with thermobarometric results (Acquafredda et al., 2008). So the increase of $D_{REEzrn/grt}$ from zircon cores dated 339 Ma and 336 Ma to zircon cores dated 323 Ma in garnet core-outer core combinations (**Fig.8**) might reflect, in line with experiments of Rubatto and Hermann (2007), decrease of T and P. This is reinforced by the similar trend of the inner rim of zircon from the matrix dated 305 Ma.

Ambiguity appears when we consider the other rims giving ages 296 Ma-300 Ma (**Fig.8**) and formed during cooling at T≅700°C out of the T range explored by experiments. The $D_{REEzrn/grt}$ values in this case decrease. On the other hand, the fact that rims of garnet and zircon show increase and decrease of HREE, respectively, proves disequilibrium. The disequilibrium between the zircon rim and the armouring garnet rim suggests that the zircon rim formed earlier than garnet rim, which subsequently broke down producing corona.



7. CONCLUSION

The results of the present study taking into account REE distribution in garnet, zircon and orthopyroxene, as well as P-T path, allow to interpret with confidence the U-Pb results:

(1) Zircon core from matrix giving concordant age at 334±12 Ma, apparent subconcordant ages of 336±10 and 339±11 Ma and concordant ages around 323 Ma produce $D_{HREEzrc/grt}$ approaching equilibrium from Tb to Lu when combined with the core-outer core region of the garnet (**Fig.8a-8b**). The orthopyroxene from matrix combined with core-outer core region of garnet shows $D_{HREEopx/grt}$ suggestive of equilibrium from Er to Lu (**Fig.7**) indicating that granulite facies conditions were stable at that time.

(2) The zircon 10 in corona shows resorbed sub-euhedral core preserving zoning, which has the highest contents in Th, U and HREE which are highly fractionated (Yb_N/Gd_N=11.44). Its Th/U ratio is high (0.51) and it shows positive anomaly of Ce and negative anomaly of Eu. These features are compatible with precipitation from a melt. The outer core of this zircon dated 323±8 Ma approaches equilibrium from Er to Lu with outer core of garnet. Since metasediments and metabasic rocks of the lower part of the deep crust of the Serre section underwent partial melting, this age could indicate that anatexis or interaction with melts occurred. Interestingly, even some mafic dikes were emplaced at *323±5 Ma* (Fornelli et al. submitted) within the metapelites overlying the felsic granulites hosting the rock of the present example.

(3) The overgrowths dated 305 Ma, 300 Ma and 296 Ma in matrix and structurally similar overgrowths on zircon grains from corona and garnet rim, likely suggest they formed earlier than the armouring garnet rim and, obviously, before the formation of the corona resulting in disequilibrium with the rim of garnet. Thermobarometric data indicate that corona around garnet

in rocks of the lower portions of the Serre section formed under decompression (Acquafredda et al., 2008). However the metamorphic stage that later partially consumed garnet is not timely registered by zircon data in this sample. Some indications derived from zircon ages around 280 Ma, in other metabasites of the Serre crust section (Fornelli et al submitted).

Accordingly, better constrained contribution to P-T path results in the following points: the metamorphism peaked much earlier than previously assumed around 350 Ma (versus 300 Ma in Schenk 1984, 1989; Micheletti et al., 2008) and the multistage Variscan decompression after the metamorphic peak in Southern European Variscides (323 Ma-300 Ma in Acquafredda et al., 2008) lasted tens millions of years at least locally up to formation of garnet rim and its consumption (280 Ma?) (**Fig.10**).

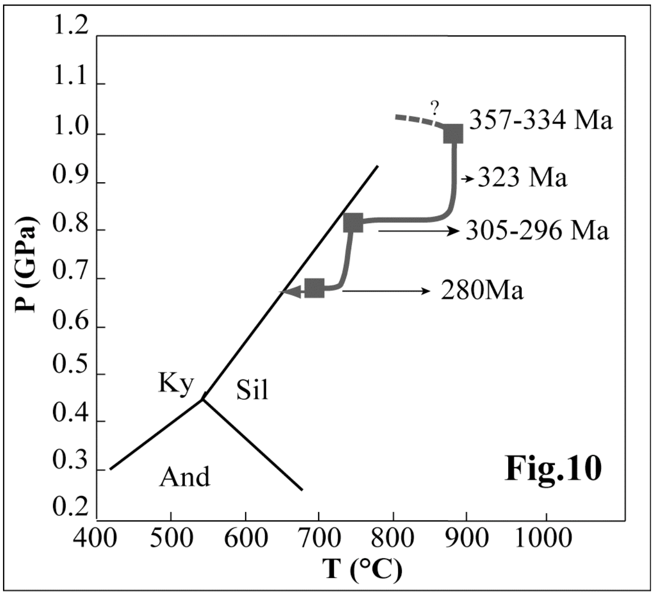


Fig.10