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2008 J. Phys.: Conf. Ser. 121 022002

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## Garnet growth in natural high pressure regime: a key tool in unravelling the pressure-temperature path of rocks involved in mountain belt orogeny

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**Abstract.** A study of a natural system concerning the growth of minerals (garnet) into metapelite host rocks from Calabria (southern Italy), which underwent pressure up to 1.2 GPa, is presented. Through the application of a thermodynamic model it was possible to determine P and T conditions achieved during metamorphic evolution of these rocks useful to reconstruct the related tectonic settings of poly-orogenic metamorphic complexes.

### 1. Introduction

Subduction of oceanic lithosphere and continental collision, occurring during the plate convergence, represent the most significant examples of natural system in which crustal rocks can achieve high pressure (HP) metamorphic conditions. In this scenario, entire crustal sectors are shifted to deeper levels up to 60-70 km, where they constitute the roots of orogenic mountain belts. In such environments, new crystalline phases as well as indicative polymorphs occur. At the same time, other minerals change their composition during growth. This is strictly dependent on environmental conditions, and as a consequence compositional trends within mineral phases reveal information about experienced P and T metamorphic conditions.

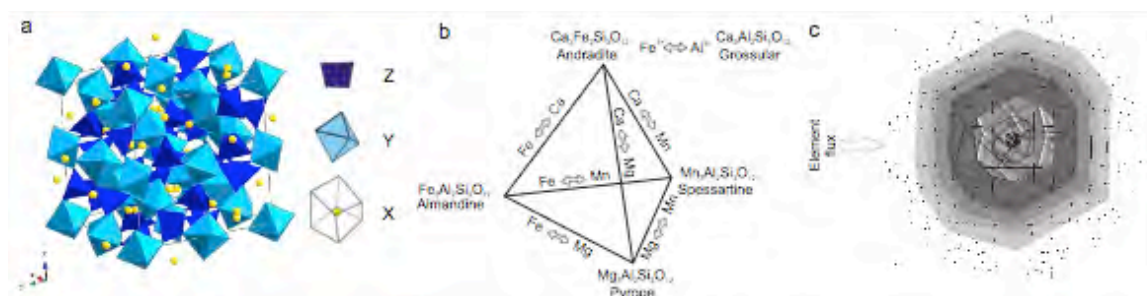
Garnet represents one of the most common minerals used as tracer of P-T changes. It is normally found both in gneissic- and schistose-type metamorphic rocks derived from argillaceous protolith, as well as in magmatic-derived rock, always due to the effects of high-pressure and high-temperature conditions.

Garnet is a marker of changes occurring during metamorphic evolution, because of its very sensitive composition to pressure and temperature variations. In addition, cation diffusion within its crystalline framework is sufficiently slow to preserve compositional differences within a grain. For the above reasons, it represents a key mineral in interpreting the genesis of many metamorphic rocks via geothermobarometry applications.

The structural formula of garnet is characterised by three different sites ( $X_3Y_2Z_3O_{12}$ ) occupied by cations in the following ways: a) X is 8-coordinated (distorted cubic) site that incorporates Ca, Mn,

Fe<sup>2+</sup> and Mg; b) Y is a small 6-coordinated (octahedral) site that incorporates Al, Fe<sup>3+</sup> and Cr<sup>3+</sup>; c) Z is a tetrahedral site where generally Si allocates (Figure 1a).

Most of common garnets are characterised by an ideal solid solution among the following endmembers: almandine (Fe<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>), pyrope (Mg<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>), spessartine (Mn<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>) plus grossular (Ca<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>), even if the relatively high fO<sub>2</sub> values can lead to the formation of Fe<sup>3+</sup> endmember (andradite - Ca<sub>3</sub>Fe<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>) as schematically reported in Figure 1b.



**Figure 1.** a) 3-D crystal framework of garnet. The octahedral and tetrahedral sites are occupied by Al, Fe<sup>3+</sup>, Cr<sup>3+</sup> and Si, respectively. Circles represent the bivalent cations (Ca, Mn, Fe<sup>2+</sup>, Mg) placed in the distorted cubic site; b) Composition space of garnet showing the compositional exchange vectors of the garnet solid solution series; c) Schematic representation of a possible relative concentration gradient around a garnet porphyroblast.

## 2. Garnet as a natural geobarometer

Natural garnet growth depends on several parameters, which operated during the tectono-metamorphic evolution of the Earth crust. Compositional changes during growth (i.e. zoning) preserved in garnet crystals are interpreted as an evidence for fractional crystallisation, which changed the chemical composition of the matrix around the crystals during its growth [1] (Figure 1c). The chemical composition of the matrix around garnet crystals depends on the amounts of elements fractionated into the mineral and on the element flux into the matrix volume [2, 3]. If fractional crystallisation of garnet in a given matrix volume is faster than the transport of garnet nutrients (Figure 1c) into this volume, the composition of the matrix reservoir is progressively depleted in elements fractionated into the garnet crystal [4]. These phenomena are significantly controlled by the variation of  $\Delta P/\Delta T$  ratio, strictly connected to different geothermal gradient occurring during the evolution of plate geodynamics. Garnet zoning, developed during crystal growth, represents the response of a natural system (here identified by the bulk rock chemistry considered to be in equilibrium – i.e. the effective bulk composition described in ref [5]) to P-T variations.

Since garnet constitutes a very widespread mineral in rocks metamorphosed at HP conditions, its chemical variations become a useful tool for geobarometric estimates, able to unravel the tectono-metamorphic history of the mountain belts.

It is worth noting that the above considerations are based on the formal thermodynamic relationship among pressure, temperature and mineral composition that forms the basis of all calculations of mineral equilibria as a function of these variables (Equation 1).

$$\Delta G_R = 0 = \Delta H_{298,1} + \int_{298}^T \Delta C_P \cdot dT + \int_1^P \Delta V \cdot dP - T \left( \Delta S_{298,1} + \int_{298}^T \frac{\Delta C_P}{T} \cdot dT \right) + RT \ln K \quad (1)$$

The terms  $\Delta G$ ,  $\Delta H$ ,  $\Delta S$ ,  $\Delta V$ ,  $\Delta C_P$  are the free energy, enthalpy, entropy, volume and heat capacity of reaction, respectively. K represents the constant of equilibrium, which is function of the activity

coefficient of the reactants/products ratio of a reaction. At equilibrium, the free energy of reaction must be zero.

There are two general methods applied for solving the metamorphic petrology problems:

1. Calculations by using a single equilibrium relation of the form of Equation 1. In some applications two or more are combined and solved simultaneously for parameters such as pressure and temperature. Conventional geothermometry and geobarometry are examples of this type of approach.
2. Calculations that utilize a set of equations of the form of Equation 1 that completely define the phase equilibria of the system. These types of calculations permit simultaneous calculations of the compositions of all minerals in the same assemblage at equilibrium at any values of P and T.

In the former case, the goal of geothermobarometry is to infer the conditions at which one rock equilibrated, by determining the equilibrium constant to be used in the equation for calculation of T (at fixed P) and P (at fixed T) or both. The basic method of geothermobarometry is very straightforward. Values of  $\Delta H$ ,  $\Delta S$ ,  $\Delta C_p$ , and  $\Delta V$  are known from experimental calibrations or published thermodynamic data. Within a rock, the value of the equilibrium constant is obtained by determining the compositions of coexisting minerals (i. e. mineral paragenesis) by means of an electron microprobe (EPMA). Analytical data are then used to draw a line of constant equilibrium on a P-T diagram and it is inferred that the sample must have equilibrated somewhere along this line. If two different equilibria can be evaluated then two lines of constant equilibrium can be drawn on the P-T diagram and the intersection of the two lines defines a single pressure and temperature value of equilibrium.

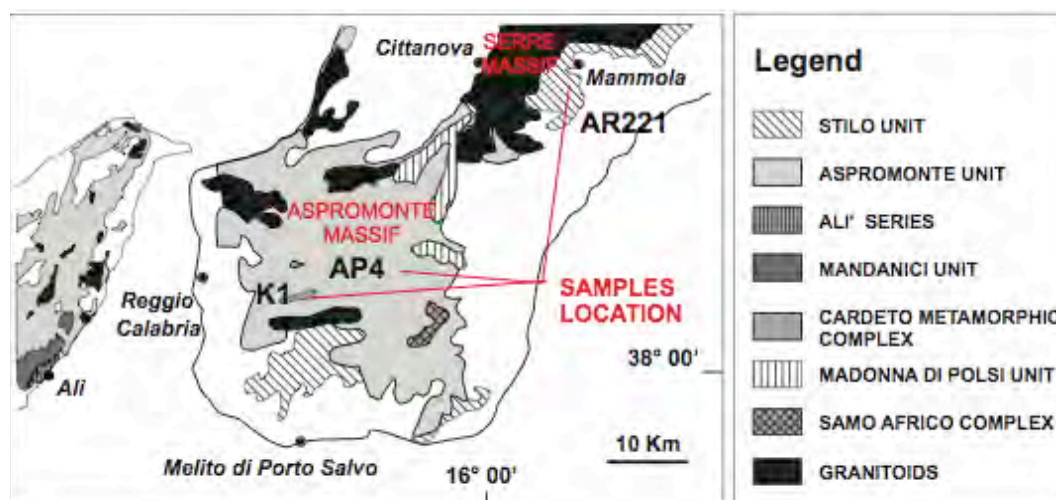
In the latter case it is possible to infer calculations that incorporate only the equations of chemical equilibrium (Equation 1), and calculations that incorporate both the equations of chemical equilibrium and the equations of mass balance. In this last case, it can be possible to ascertain the intensive variables T, P and mineral composition, as well as the mineral abundances within the system (modes). Moreover, the equilibrium assemblage as a function of rock bulk composition can be examined.

Furthermore, theoretical predictions of representative equilibrium assemblages, supported by petrological and chemical observations, can provide a series of P-T paths by using equilibrium-phase relations calculated by free energy minimisation for a system of specific bulk composition (i.e., pseudosection calculation method - [6, 7, 8]). For each sample, the P-T history is detailed by combining petrological and rock-textural information of the studied garnets.

Even if the above method seems to entirely overcome the intrinsic contradictions related to conventional geothermobarometry, mainly based on exchange reactions among minerals in different domains of a single rock [9] calculated at specific experimental conditions, several sets of limitations must be considered in order to achieve reliable results.

In particular it is important to take into account: a) the reliability of the thermodynamic data from available datasets; b) errors in the effective bulk composition used in the calculation [5]; e) extreme simplification of solid solution models of some minerals like garnet.

In the present study we considered three garnet bearing rocks with comparable bulk chemical composition (Table 1a), collected into three distinct areas of the southern sector of Calabria-Peloritani Orogen (Figure 2). The P-T evolution is achieved by intersection of garnet isopleths (i.e. iso-compositional curves) of garnet bearing metapelites using the thermodynamic modelling via P-T pseudosections [8].



**Figure 2.** Geological sketch map of the Aspromonte and Serre Massifs in southern Italy (modified after [12]) and location of collected garnet bearing samples.

**Table 1a.** XRF-bulk rock analyses of metapelite samples in the simplified chemical system MnNCKFMASH.

Location	Serre Massif	Aspromonte Massif	
Sample	AR221	K1	AP4
Lithotypes	Paragneiss	Micaschist	Paragneiss
MnO	0.19	0.06	0.11
Na <sub>2</sub> O	3.43	0.73	1.00
CaO	3.91	0.45	0.16
K <sub>2</sub> O	3.38	4.66	4.00
FeO <sup>tot</sup>	7.11	6.94	7.85
MgO	2.81	2.33	1.76
Al <sub>2</sub> O <sub>3</sub>	22.18	22.75	20.23
SiO <sub>2</sub>	56.99	62.08	64.89

**Table 1b.** End-member values from chemical composition of garnet point analyses.

Sample	Garnet zone	Point analyses	Alm %	Grs %	Sps %	Pyr %
AR221	Grt1	A1	56	27	12	3
	Grt2	A2	64	23	8	5
	Grt3	A3	61	9	23	7
K1	Grt1	B1	69	12	15	3
	Outer Grt1	B2	77	14	2	7
	Grt2	B3	85	6	7	2
AP4	Grt1	C1	84	3	13	10
	Inner Grt2	C2	55	22	20	3
	Outer Grt2	C3	55	24	18	3

### 3. The solution of geological problems via thermodynamic modelling approach: a case study

The Calabria Metamorphic basement represents a natural laboratory to investigate and describe several types of garnet bearing rocks which often reflect a multi-stage metamorphic evolution developed during different orogenic cycles.

As already evidenced, in our study we considered three garnet typologies, which belong to metapelite samples from the Aspromonte and Serre Massifs located in the southern sector of the Calabria Peloritani Orogen (Figure 2).

**Table 2.** Summary tables of the solid solution models with brief commentary

Name and phase of solution model	End members
Biotite - Bio (HP)	Mn-biotite - Mnbi $\text{KMn}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$
	Annite - Ann $\text{KFe}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$
	Phlogopite - Phl $\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$
	Eastonite - East $\text{KMg}_2\text{Al}_3\text{Si}_2\text{O}_{10}(\text{OH})_2$
	mnts_i $1\text{east}+2/3\text{mnbi}-2/3\text{phl}$
	sdph_i $1\text{east}+2/3\text{ann}-2/3\text{phl}$
Garnet - Gt (HP)	Almandine - Alm $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$
	Grossular - Grs $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$
	Spessartine - Sps $\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$
	Pyrope - Pyr $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$
Chlorite - Chl (HP)	Mn-Chlorite - Mnchl $\text{Mn}_{10}\text{Al}_4\text{Si}_6\text{O}_{20}(\text{OH})_{16}$
	Daphnite - Daph $\text{Fe}_{10}\text{Al}_4\text{Si}_6\text{O}_{20}(\text{OH})_{16}$
	Amesite - Ames $\text{Mg}_8\text{Al}_8\text{Si}_4\text{O}_{20}(\text{OH})_{16}$
	Clinochlore - Clin $\text{Mg}_{10}\text{Al}_4\text{Si}_6\text{O}_{20}(\text{OH})_{16}$
Epidote - Ep (HP)	Clinzoisite - Czo $\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})$
	Fe-epidoto - Fep $\text{Ca}_2\text{Fe}_2\text{AlSi}_3\text{O}_{12}(\text{OH})$
White Mica - Pheng (HP)	Celadonite - Cel $\text{KMgAlSi}_4\text{O}_{10}(\text{OH})_2$
	Fe-Celadonite - Fcel $\text{KFeAlSi}_4\text{O}_{10}(\text{OH})_2$
	Muscovite - Mu $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$
Plagioclase - AbPl	Anortite - An $\text{CaAl}_2\text{Si}_2\text{O}_8$
	High albite - Abh $\text{NaAlSi}_3\text{O}_8$
Feldspar - feldspar	K-feldspar - Kfs $\text{KAlSi}_3\text{O}_8$
	Anortite - An $\text{CaAl}_2\text{Si}_2\text{O}_8$
	High albite - Abh $\text{NaAlSi}_3\text{O}_8$
Glaucophane - Gl	Glaucophane - Gl $\text{Na}_2\text{Mg}_3\text{Al}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$
	Fe-Glaucophane - Fgl $\text{Na}_2\text{Fe}_3\text{Al}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$
Chloritoid - Ctd (HP)	Mn-Chloritoid - Mnctd $\text{MnAl}_2\text{SiO}_5(\text{OH})_2$
	Fe-Chloritoid - Fctd $\text{FeAl}_2\text{SiO}_5(\text{OH})_2$
	Mg-Chloritoid - Mctd $\text{MgAl}_2\text{SiO}_5(\text{OH})_2$
Staurolite - St (HP)	Mn-Staurolite - Mnst $\text{Mn}_4\text{Al}_{18}\text{Si}_{7.5}\text{O}_{48}\text{H}_4$
	Fe-Staurolite - Fst $\text{Fe}_4\text{Al}_{18}\text{Si}_{7.5}\text{O}_{48}\text{H}_4$
	Mg-Staurolite - Mst $\text{Mg}_4\text{Al}_{18}\text{Si}_{7.5}\text{O}_{48}\text{H}_4$

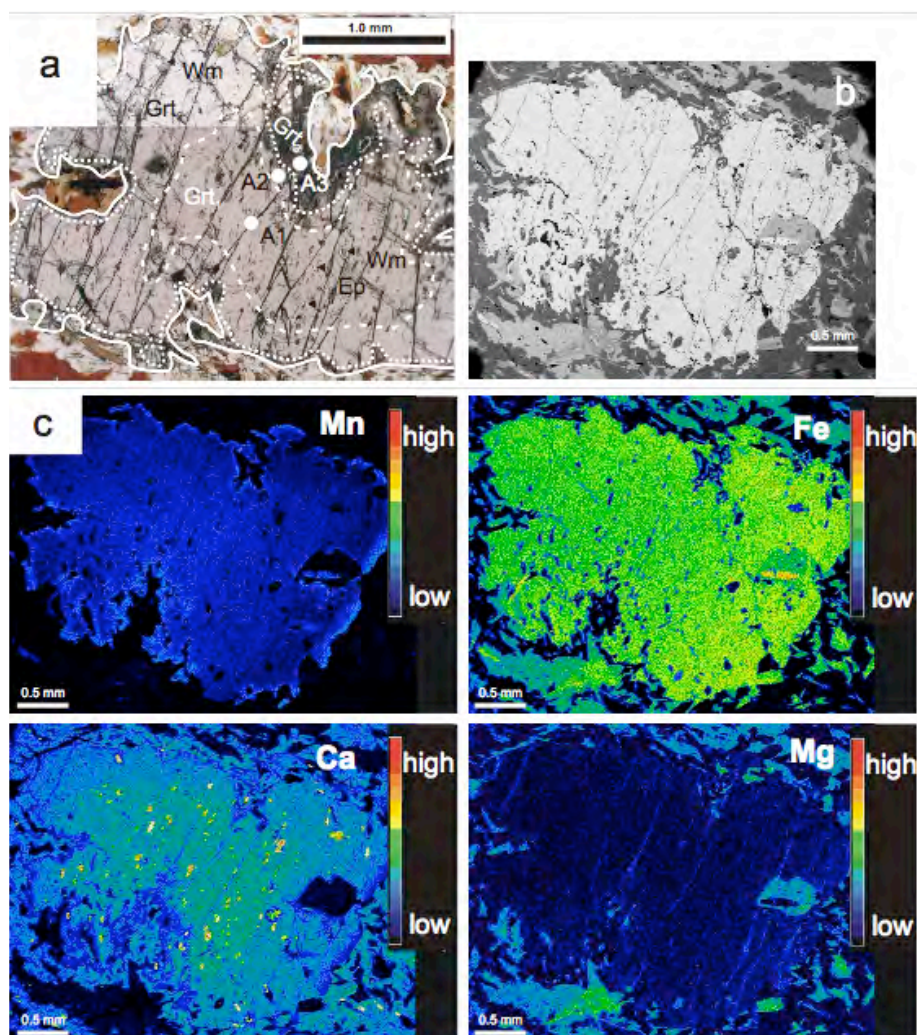
The Aspromonte and Serre Massifs represent two fragments of the upper Paleozoic suture produced by the plate convergence of North America, Europe, Asia and Gondwana. This collision, which have caused the so called Hercynian orogenesis (from 390 to 310 Ma), brought to the formation

of a super-terrane known as Pangea and was responsible for the production of the main metamorphic complexes outcropping in the two Massifs.

The successive geodynamic evolution of this chain sector was characterised by thinning of continental crust and consequent opening of Tethys Ocean around 250 Ma. The subsequent closure of the Tethys gave rise to the formation of the Alpine orogenic belt (from 100 to 25 Ma).

The dominant features characterising these orogenic events are: High T/Low P and Low T/High P ratio for the Hercynian and the Alpine orogeny, respectively.

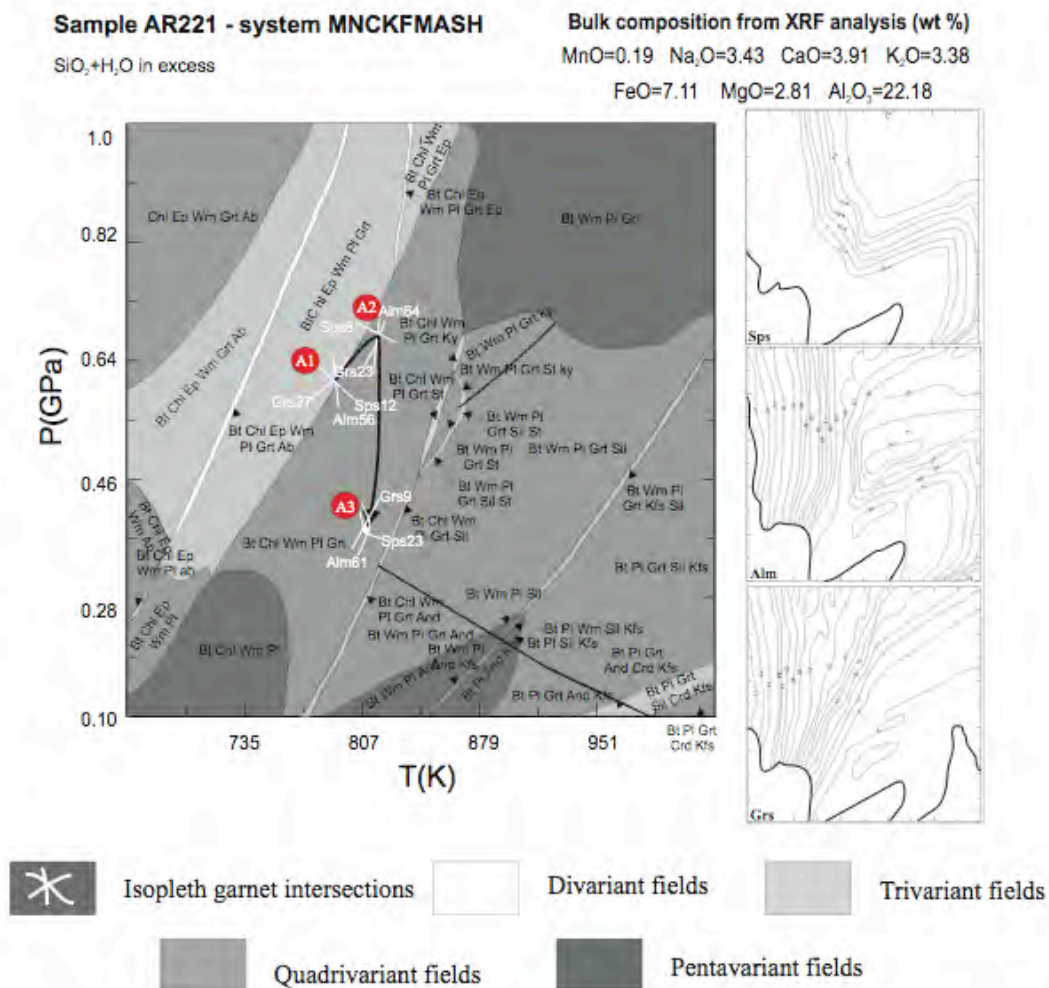
In this scenario, the Hercynian geological relics are still well preserved in the metamorphic basement of the Serre Massif. Differently, the present-day geological framework of the Aspromonte Massif is the result of the subsequent Alpine orogenesis, which in part reworked the relic Hercynian terrains, affecting at the same time part of the overlaying Mesozoic sedimentary cover.



**Figure 3.** Hercynian-type garnet from a metapelite of the Serre Massif (AR221 sample) characterised by two progressive steps of growth (Grt1 – Grt2), followed by embayments of garnet rim (Grt3), which testify resorption during retrogression. **a)** micro-photograph at thin section scale, **b)** BSE image of investigated garnet, **c)** EDS X-ray maps (Ca, Mn, Mg and Fe) of selected garnet.

In this composite tectonic setting, the investigation of compositional variation in garnet, represents one of the most reliable key tool to unravel the different effects of the Alpine- (high  $\Delta P/\Delta T$ ) and Hercynian-orogenesis (low  $\Delta P/\Delta T$ ).

The P-T evolution of the collected garnet bearing metapelites was yielded by means of P-T pseudosections (phase diagram calculated at constant bulk composition). In particular, for each specimen we started with a multiple approach, which lead to computation of microscopic observations at the thin section by means of optical petrographic microscopy, and continued with the use of Scanning Electron Microscope equipped with EDS spectrometer for the acquisition of BSE images and elaboration of X-ray maps of garnets (Figures 3, 5, 7). Indeed, X-ray fluorescence (XRF) spectrometry was employed to define the bulk-rock chemistry useful to calculate the specified pseudosection for each sample, using free energy minimisation approach by ref [8]. This approach, based upon the approximation that the variable solid solution compositions of a single mineral phase can be simplified by a series of arbitrarily defined components (i.e. pseudocompounds), treats with solutions up to 3 independent mixing sites and up to 3 species mixing on each site [10].

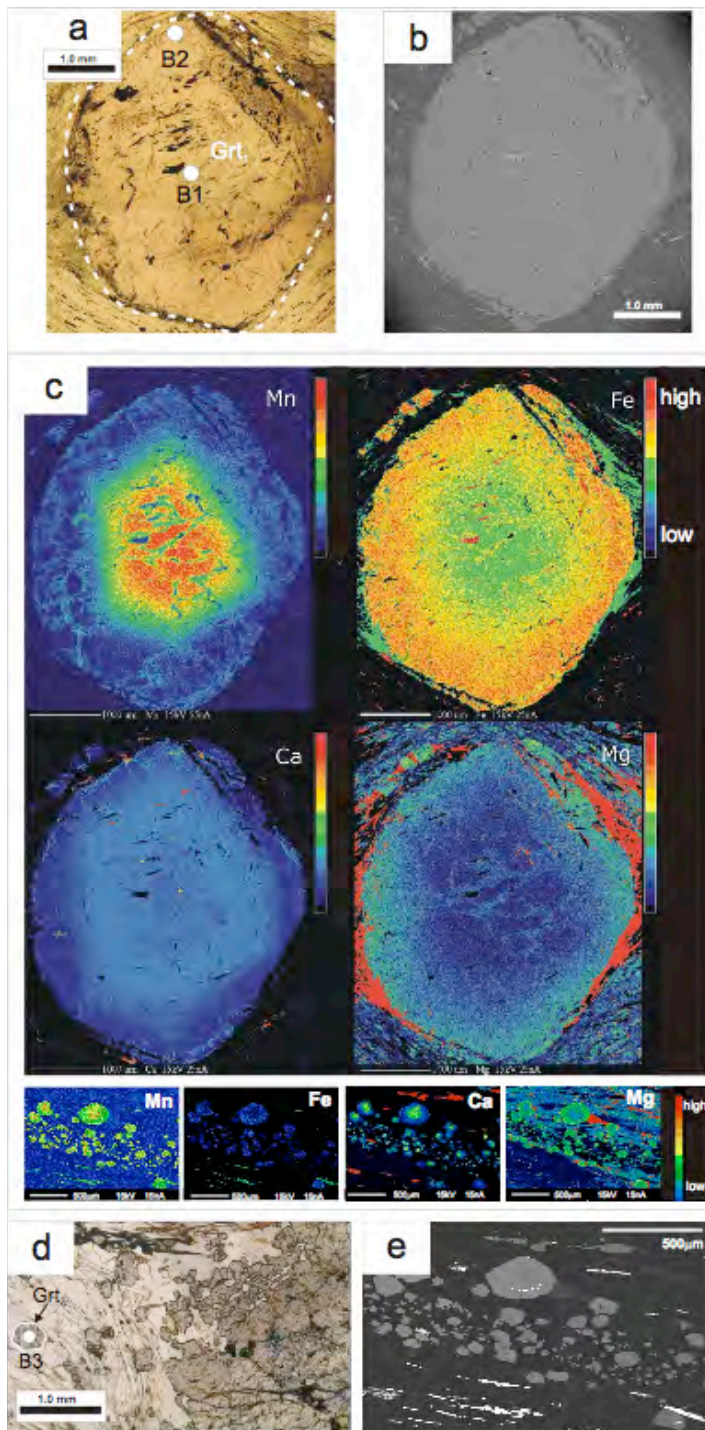


**Figure 4.** P-T pseudosection of AR221 sample in MnNCKFMASH system and garnet isopleths P-T constraints. H<sub>2</sub>O and quartz computed to be in excess. Black arrow: P-T path.



The accuracy of this approximation is related to the choice of the appropriate solid solution model (Table 2) and the relative spacing of the pseudocompounds in the compositional range (i.e. solid solution model dataset), which can be controlled by the user.

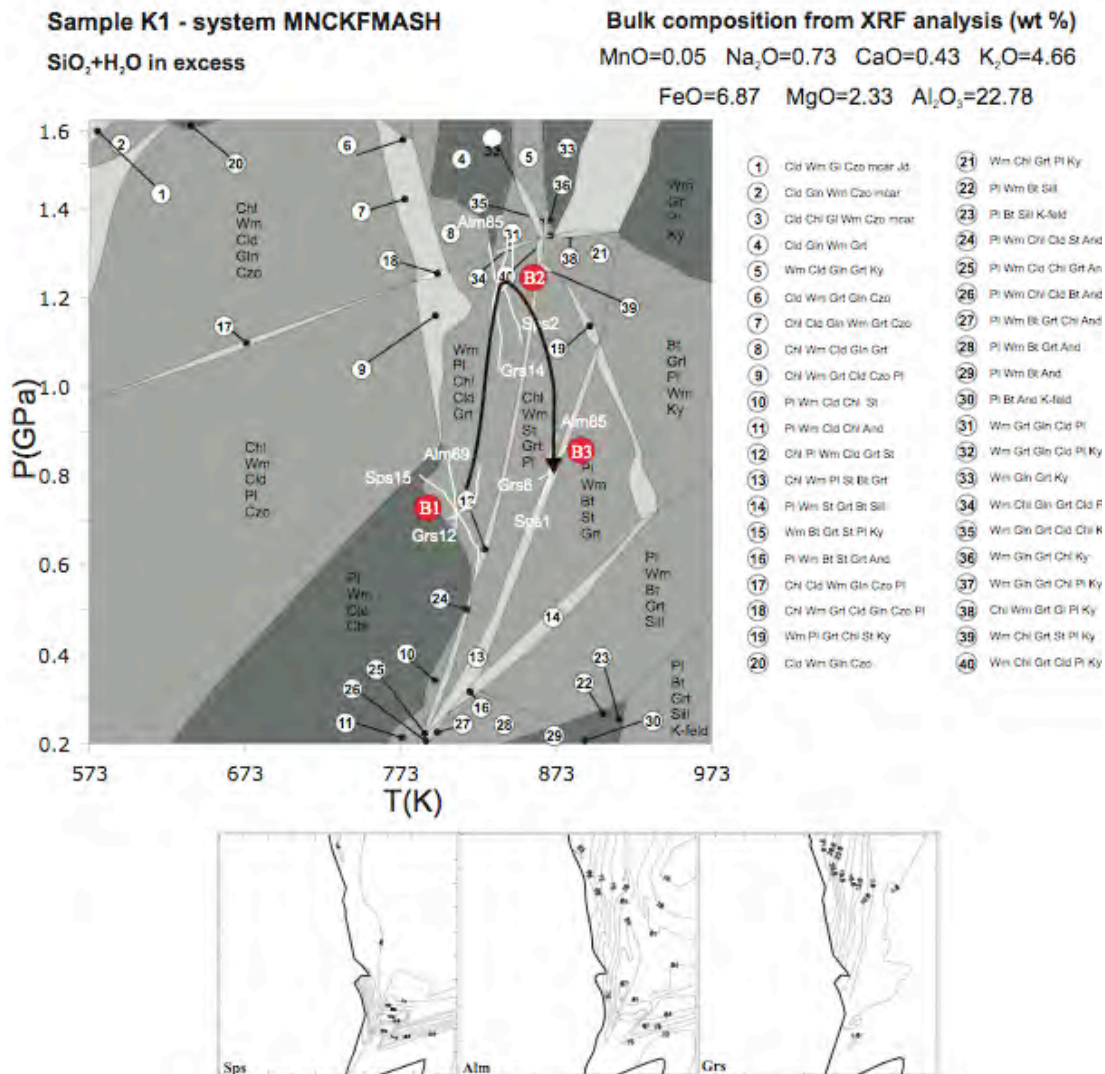
The preservation of concentric compositional shells developed during the multi-stage garnet growth of the collected samples permitted us to infer evolution of the host rocks, constraining the P-T values by means of the intersection of garnet isopleths.



**Figure 5.** Alpine-type garnet from a metapelite of the Aspromonte Massif (K1 sample), characterised by a first garnet generation represented by large crystals (Grt1), followed both by rim crystal growth and small garnets with different composition (Grt2). **a)** photograph at thin section scale, **b)** BSE image of investigated garnet, **c)** EDS X-ray maps (Ca, Mn, Mg and Fe), which show a compositional zoning patterns for Grt1 garnet, and a concentric chemically zoned composition of Grt2 garnet.

All of the examined rocks exhibit very similar chemical composition; this fact minimises the effects of bulk composition and allows one to make a comparison between garnets belonging to rocks that, even though similar in composition (Table 2), experienced different metamorphic histories.

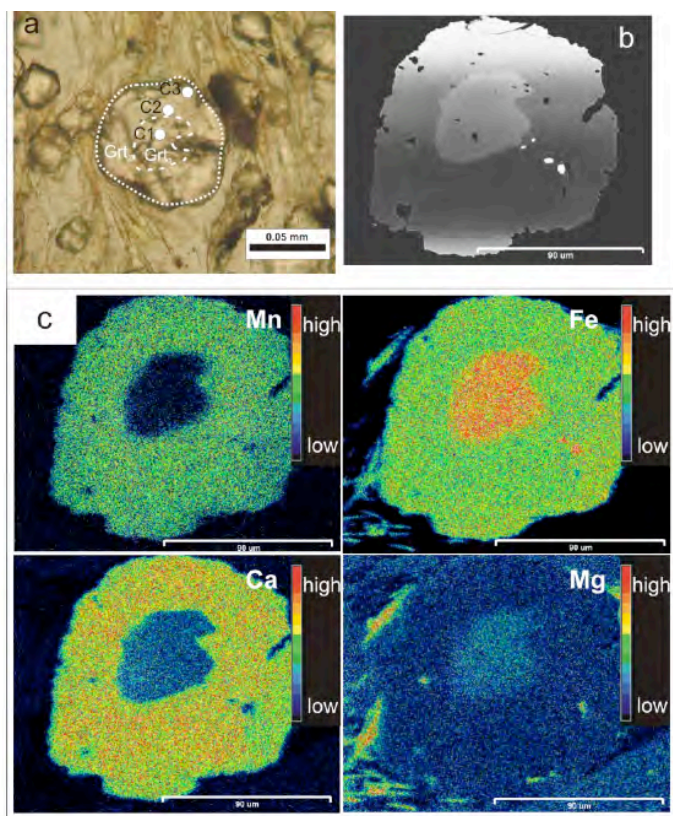
The first example is a Hercynian-type garnet from a metapelite specimen collected in the Serre Massif (sample AR221 – Figure 2). In this sample, garnet is characterised by a first growth step represented by inner core grown at expenses of epidote, chlorite and white mica, followed by a subsequent growth stage represented by outer core grown at expenses of chlorite and white mica. Petrographic evidence of embayments in garnet rim suggests resorption during the P-T decreasing probably linked to the exhumation of the rock (Figure 3).



**Figure 6.** P-T pseudosection of K1 sample in MnNCKFMASH system and garnet isopleths P-T constraints. H<sub>2</sub>O and quartz computed to be in excess. Black arrow: PT path. Legend on figure 4.

Intersection among isopleths of garnet core composition, evolving from inner core composition of Alm<sub>56</sub>Grs<sub>27</sub>Sps<sub>12</sub>Pyr<sub>3</sub>, to an outer core composition of Alm<sub>64</sub>Grs<sub>23</sub>Sps<sub>8</sub>Pyr<sub>5</sub>, allowed to constrain P-T values ranging from 0.61 to 0.68 GPa and from 789K to 825K pertaining to a crustal thickening event probably related to the early Hercynian compressional event. The rim compositions ranging from

Alm<sub>64</sub>Grs<sub>13</sub>Sps<sub>17</sub>Pyr<sub>7</sub> to Alm<sub>61</sub>Grs<sub>9</sub>Sps<sub>23</sub>Pyr<sub>7</sub>, provided pressure values of 0.56 GPa and 0.40 GPa at peak or slightly decreasing temperature suggesting a *quasi*-isothermal decompression event at about 0.28 GPa as the result of uplift and exhumation (Figure 4).



**Figure 7.** Example of poly-orogenic garnet nucleation from a metapelite of the Aspromonte Massif (AP4 sample), displaying a relic metamorphic evolution preserved in a small Hercynian garnet cores (Gr1), overprinted by a subsequent Alpine type garnet overgrowth (Gr2). **a)** photograph at thin section scale, **b)** BSE image of investigated garnet, **c)** EDS X-ray maps (Ca, Mn, Mg and Fe) of selected garnet, clearly showing the evident double discontinuous stages of crystallisation.

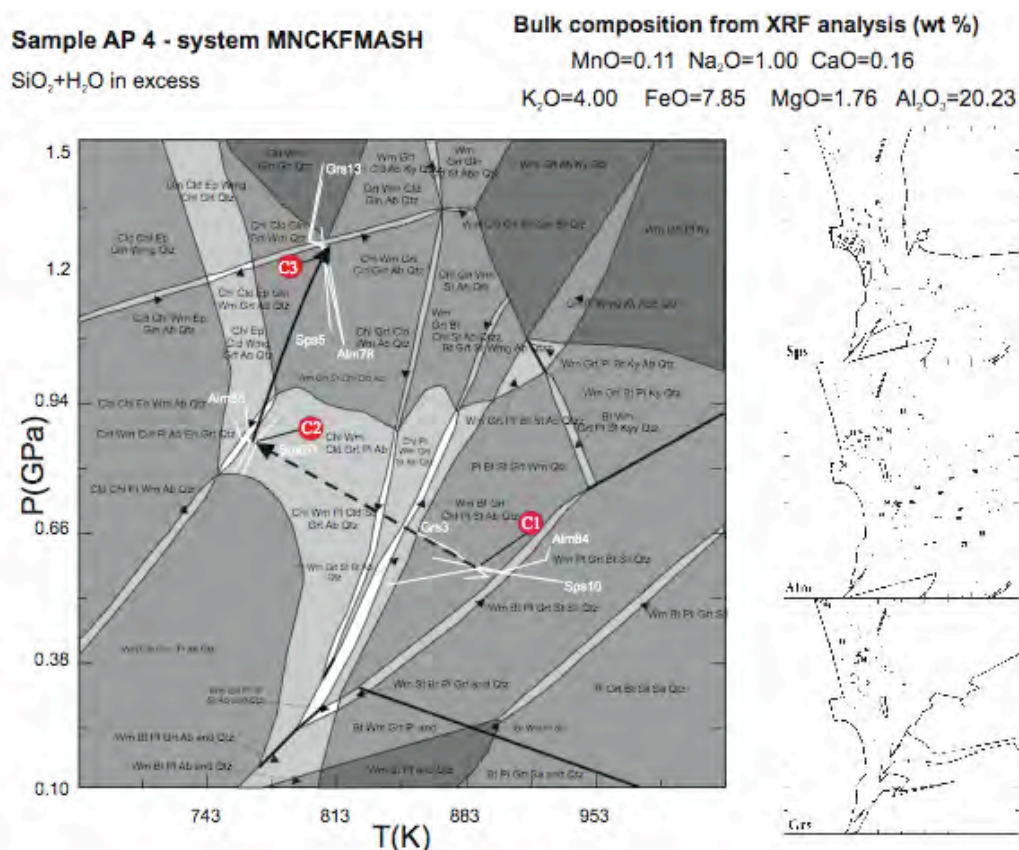
The second example (sample K1 – Figure 2) corresponds to an Alpine-type garnet because of the high  $\Delta P/\Delta T$  ratio revealed by its thermobarometric evolution. In particular, at least two stages of growth are well documented in this rock: the first garnet generation Grt1 (Alm<sub>65-74</sub>Sps<sub>8-15</sub>Grs<sub>7-15</sub>Pyr<sub>2-12</sub>) is generally represented by large cores, actually preserved in the inner portion of crystals. X-ray map images show clearly changes in composition between adjacent concentric shells (Figure 5), allowing to constrain the P-T conditions of the prograde trajectory to 0.7GPa at 823K (Figure 6).

The outer shell of Grt1-type crystal associated with the last growth has been interpreted as the nucleation region of the new garnet crystals Grt2 (Alm<sub>65-88</sub>Sps<sub>3-6</sub>Grs<sub>4-28</sub>Pyr<sub>6-13</sub>), which testified the peak equilibrium reaction at P=1.0GPa and T=843K (Figure 6).

The third and last sample (sample AP4 – Figure 2), consisting of a Hercynian-type garnet that was subsequently overgrowth by an Alpine-type one, is characterised by a relic mineral association preserved as rare small cores of garnet in equilibrium with ilmenite inclusions and epidote. Intersection among isopleths of relic garnet cores (Alm<sub>84</sub>Grs<sub>3</sub>Sps<sub>13</sub>Pyr<sub>10</sub>), constrains the earliest P-T values (0.60±0.02 GPa – 920±20 K) interpreted as remnants of Hercynian metamorphic evolution (low  $\Delta P/\Delta T$ ).

A subsequent pervasive Alpine type high-pressure overprint characterised by new growth of idioblastic syn- to post- kinematic garnet (up to 100 μm) and/or overgrowth on the earliest Hercynian garnet cores, evolving toward the rim, to lower spessartine content compositions (Figure 7).

Isopleth intersections of new garnet, which evolve from outer core composition (Alm<sub>55</sub>Sps<sub>20</sub>Grs<sub>22</sub>Pyr<sub>3</sub>) to rim composition (Alm<sub>55</sub>Sps<sub>18</sub>Grs<sub>24</sub>Pyr<sub>3</sub>), infer P-T values ranging from 0.78 to 0.87 GPa and from 750 to 770K, highlighting the relatively high pressure overprint interpreted as the prograde path of the Alpine metamorphism (Figure 8).



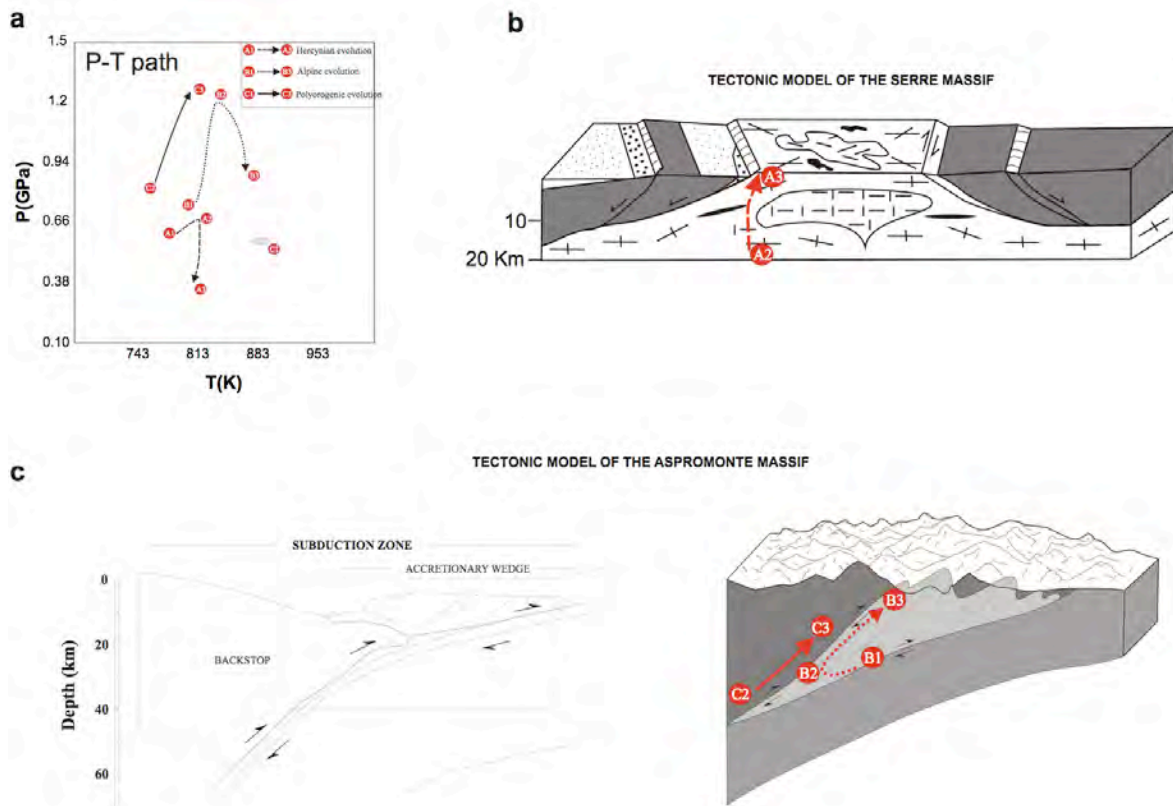
**Figure 8.** P-T pseudosection of AP4 sample in MnNCKFMASH system and garnet isopleths P-T constraints. H<sub>2</sub>O and quartz computed to be in excess. Black arrow: PT path. Black dashed arrow: PT gap between relic Hercynian and Alpine garnet growth. Legend on Figure 4.

#### 4. Final remarks and perspectives

This work is an example of thermodynamic modelling of several types of natural garnet growths useful to delineate the P-T evolution of some representative garnet bearing metapelites via P-T pseudosection method. The present day knowledge of the thermodynamic coefficients of mineral end member constituents, implemented within several internally consistent thermodynamic datasets [11], allows us to obtain a series of P-T equilibrium estimates, which highlighted how natural garnet can be considered a reliable tracer of fossil geothermal gradient.

The above evidences highlight, at the same time, how this approach is useful to solve several types of geological problems, which anyway have to be previously related to geological and petrological constraints.

As a final remark it is worth noting that thermodynamic modelling of comparable metapelite systems permitted to discriminate between various typologies of tectono-metamorphic conditions, characterised by peculiar  $\Delta P/\Delta T$  ratios. The first two examples, AR221 and K1, are characterised by relatively LP/HT (Hercynian) and HP/LT (Alpine) metamorphic history, respectively. Differently, the third metapelite specimen shows evidence of both Hercynian and Alpine metamorphism, testified by concentric poly-stage growth evolving from Low Pressure core to High Pressure garnet overgrowth.



**Figure 9.** **a)** P-T trajectories reconstructed from garnet composition of three different stages of growth for samples AR221 (circles A1, A2, A3), K1 (circles B1, B2, B3) and AP4 (circles C1, C2, C3). **b)** the tectonic model of the Serre Massif is shown with supposed trajectory followed by the sample AR221. **c)** tectonic model of the Aspromonte Massif. Different positions probably occupied by samples K1 and AP4 during their metamorphic evolution are shown.

Nevertheless, although yielded results are reliable, they have to be considered susceptible of several fonts of errors, mainly derived from: a) incomplete realisation of thermodynamic internally consistent dataset; and b) over-simplification of the solid solution models of natural minerals.

As an example, in our case, garnet is simplified as characterised only by the solid solution between four end members (Table 1b), although in nature this mineral is characterised by six different endmembers miscibility solid solution.

Indeed, since natural environments are typically open systems, it is difficult to provide a reliable correspondence between synthetic and natural systems due to the complexity of natural one, because of the huge number of parameters, which concomitantly operate during the real metamorphic evolution.

A synthetic system doesn't take into account the competitiveness between two or more different phases, which simultaneously grow in the same area of interest, as usually occurs in rocks. In this context, we think that a model garnet growth which takes into account, the free energy minimisation effects at the equilibrium conditions as well as the geometry of garnet nucleation and the effects of the surrounded matrix chemical composition, could provide reliable P-T constraints within a more detailed thermodynamic modelling of natural systems.

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