Rodingitization of mafic rocks from Central Evia (Greece) associated with serpentinite exhumation: Evidence from Petrological, Geochemical and Isotopic data

C. Karkalis [1,2], A. Magganas[1], P. Koutsovitis[3], T. Ntaflos[4]

1 National and Kapodistrian University of Athens
2 Centre for Research and Technology, Hellas (CERTH)
3 University of Patras
4 University of Vienna

Correspondence: karkalis@certh.gr, chriskark@geol.uoa.gr

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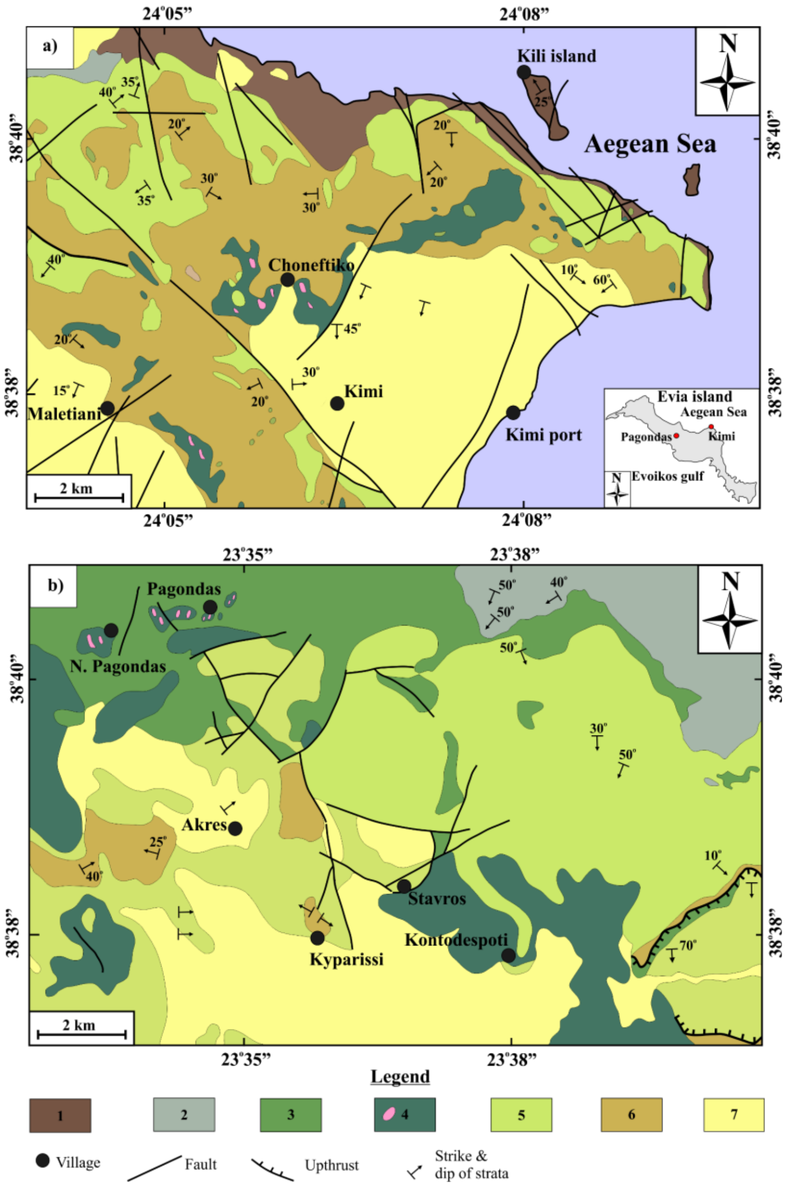


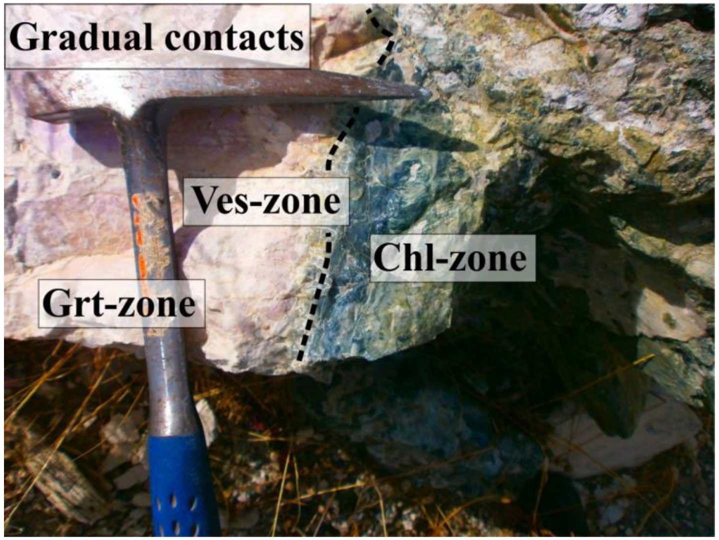
Simplified geological maps modified after Katsikatsos et al., 1981a,b

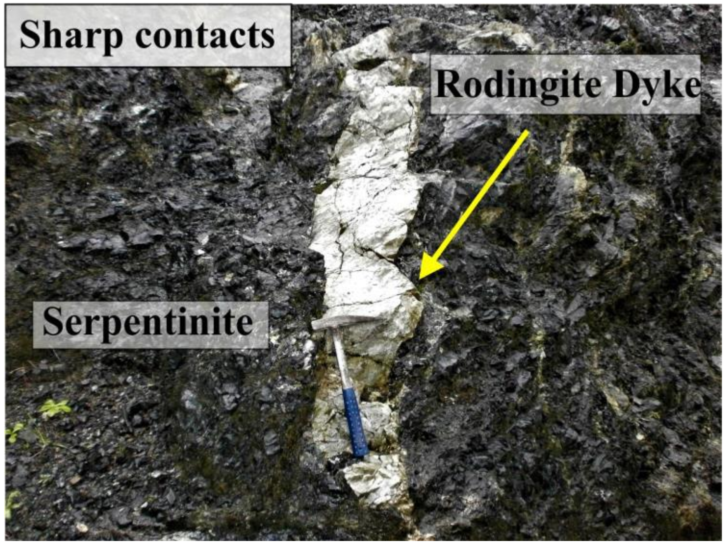
Central Evia-Geology

The **Central Evia** (Central Aegean; Greece) comprises rocks of the Pelagonian Zone that include:

- **1.** Triassic limestones & clastic sedimentary rocks
- **2.** Jurassic limestones
- **3.** U. Jurassic-L. Cretaceous ophiolitic mélange, consisting of shales, cherts, sandstones, limestone intercalations, ultramafic fragments, lateritic formations and Fe-Ni ore deposits.
- **4.** Ultramafic thrust sheets, which are intruded by **rodingite dykes and veins.** In many cases these ultramafic rocks include magnesite deposits in the form of veins and stockworks, due to the effect of carbonation processes.
- **5.** U. Cretaceous transgressive limestones
- **6.** U. Cretaceous-Paleocene flysch with limestone intercalations and blocks of ultramafic rocks, which are occasionally intruded by **rodingite dykes and veins**
- **7.** Neogene/Quaternary rocks

Field research-rodingite occurrences





- Rodingites appear in the form of dykes and/or veins intruding partly of fully serpentinized peridotites.

- These are mostly found in the **Pagondas** and **Kimi** regions of Central Evia.

- Depending on their metasomatic degree, rodingites exhibit either **sharp contacts** with their ultramafic host-rocks, or **gradual transitions**, characterized by the development of multiple zones with distinct mineralogical composition.

- In the second case, **vesuvianite** and **garnet** are mostly found in **the central zones**, whereas **clinopyroxene** and **chlorite** are mostly observed towards the rodingite **margins**.

- Metasomatic processes have in many cases affected the ultramafic host-rock creating **garnet-bearing** serpentinites and **black-wal**l (chlorite-rich) alteration zones in their contact with the rodingite dykes.

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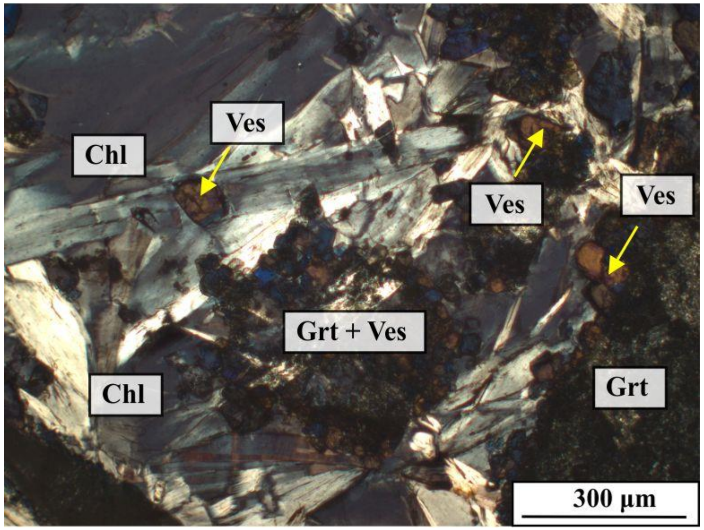
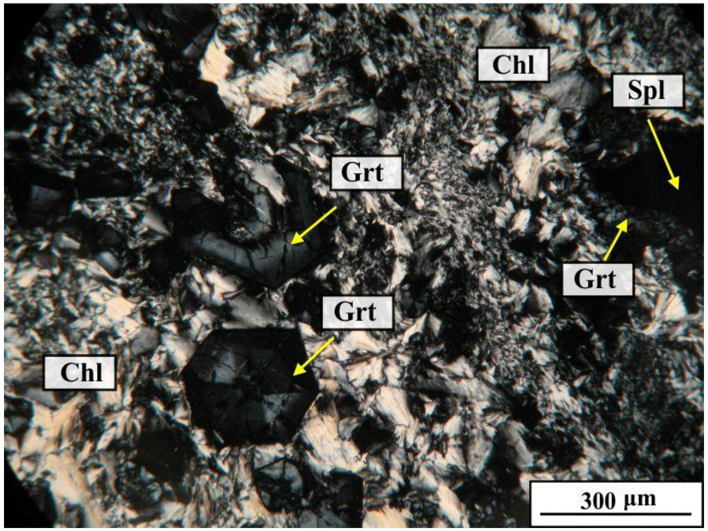
Mineralogy & Petrography





- Their **mineralogical assemblage** includes mainly: garnet + chlorite + clinopyroxene ± vesuvianite. Accessory minerals include spinel ± calcite ± prehnite ± amphibole ± orthopyroxene ± olivine ± quartz ± opaque Fe-Ti oxides.
- Their textures range mainly between **crypto-microcrystalline** to **coarse grained** usually **porphyroblastic**.
- Chlorite and garnet appear as major components of the rodingite groundmass or in the form of individual crystals.
- **Vesuvianite**, **garnet and chlorite** usually appear in the form of well-shaped **porphyroblasts.**
- **Garnet** usually exhibits oscillatory and/or hourglass **zonation**. It is classified mainly as **grossular**, whereas the **andradite-end** members are increased in the most metasomatized rodingites.
- **Clinopyroxene** appears as **neoblast** or in the form of **relict** grains in the less metasomatized rodingites.

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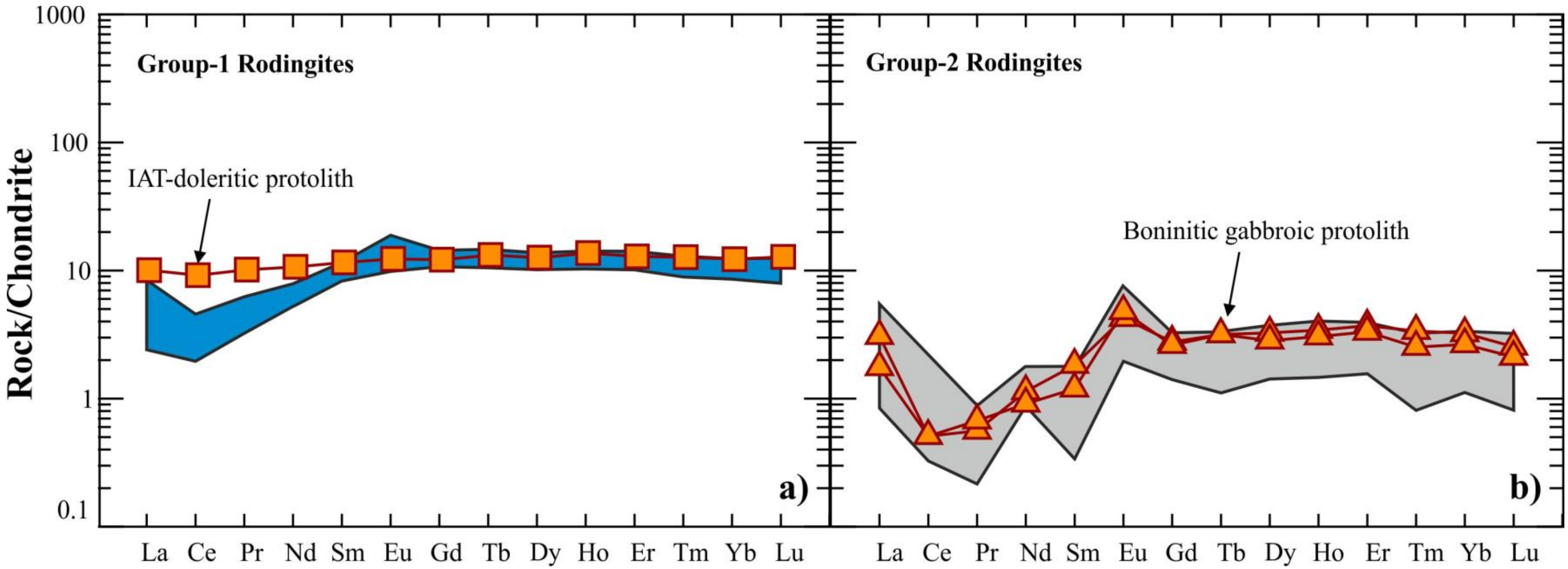
Geochemistry-Rock classification

normalizing factors from McDonough and Sun (1995)



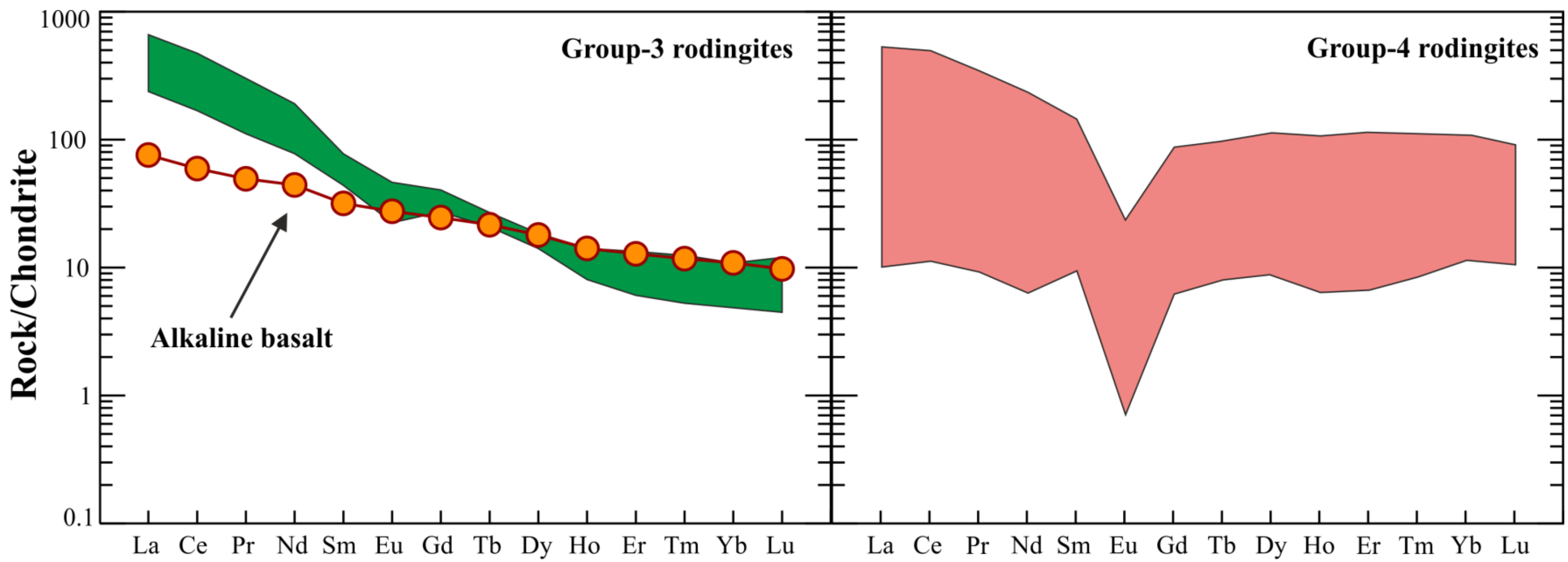
Rodingites of Central Evia resulted from extensive rodingitization of several magmatic protoliths. Several **rodingite samples**, as well as their **magmatic protoliths** (shown with orange color in the REE-patterns) were **selected**. These include: IAT-dolerite, boninitic gabbros and alkaline basalt.

- **Group-1** Rodingites (IAT-doleritic protolith): Exhibit almost flat REE patterns with positive Eu (EuCN/Eu*= 0.99-1.26) anomalies. Similar IAT-subvolcanics of Jurassic age are reported in the adjacent region of East Othris (Koutsovitis and Magganas, 2016).

- **Group-2** Rodingites (Bonninitic gabbroic protolith): Exhibit Chondrite normalized REE patterns that show strong positive Eu anomalies (Eu_{CN}/Eu*=1.69-2.97). Similar boninites of Jurassic age have been found in the adjacent regions of East Othris (Koutsovitis and Magganas, 2016) and Koziakas (Pomonis et al., 2007).

Geochemistry-Rock classification

normalizing factors from McDonough and Sun (1995)



- **Group-3** Rodingites (Alkaline basaltic protolith): Their Chondrite normalized REE patterns show significant LREE-enrichments. They present similarities with alkaline basalts that have been found in Evia & the adjacent regions of East Othris and Attica (e.g. Pe-Piper and Piper, 2002; Koutsovitis, 2012; Koutsovitis et al., 2020).

- **Group-4** Rodingites (Calc-alkaline basaltic protolith): Despite the absence of magmatic protoliths, because of extensive metasomatism, these rocks present Chondrite-normalized REE-patterns that remind calc-alkaline subvolcanic rocks form the adjacent regions of East Othris, Koziakas, Pindos and Attica (e,g, Magganas et al., 1997; Pomonis et al., 2004; Castorina et al., 2020). They also exhibit strong negative Eu anomalies (Eu_{CN}/Eu^*= 0.03-0.21).

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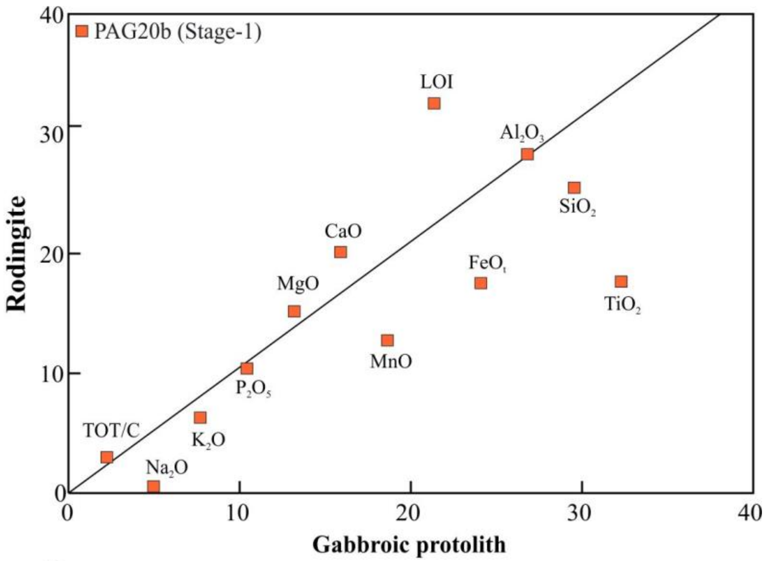
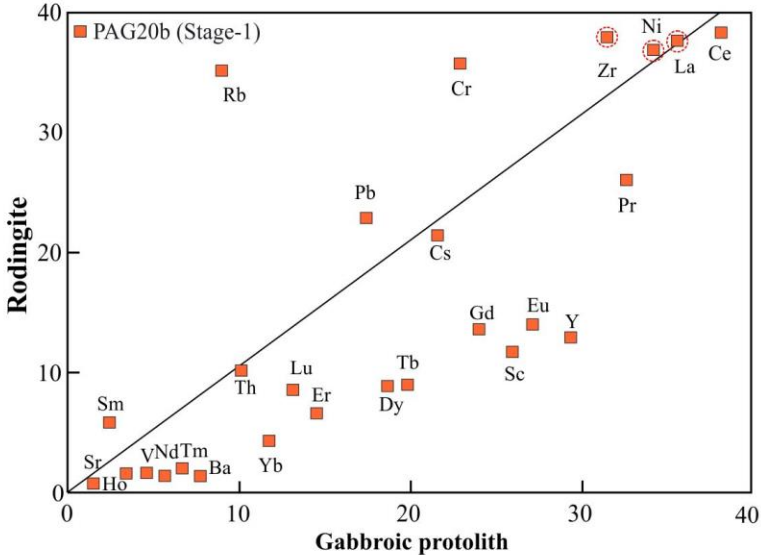
Evolution of Metasomatism & element mobility





- Rodingitization in Central Evia was evolved in **three** successive **stages** of increasing metasomatic degree.

- **Stage-1:** Initiation of rodingitization processes. This stage is associated with the dissolution of clinopyroxene from the ultramafic host rocks and the formation of Ca-rich metasomatic fluids.

- **Mineralogy:** this stage is characterized by the development of grossular, diopside, chlorite and prehnite.

- **Element mobility:** Regarding Al as immobile, Ca, LOI were increased, whereas Si and total alkalis were depleted. Most of the REE including Y were depleted.

- **Mineral reactions:**

Prehnite formation (Coleman, 1967):

$1.5An + 0.5Ca^{+2} + 1.5H_2O \rightleftarrows Prh + 0.5Al_2O_3 + H^+$ (1)

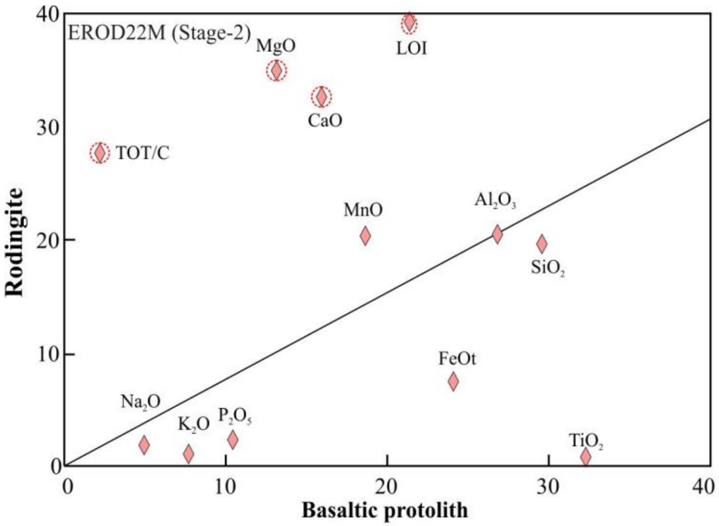
Formation hydrogrossular, chlorite & diopside (Li et al., 2008):

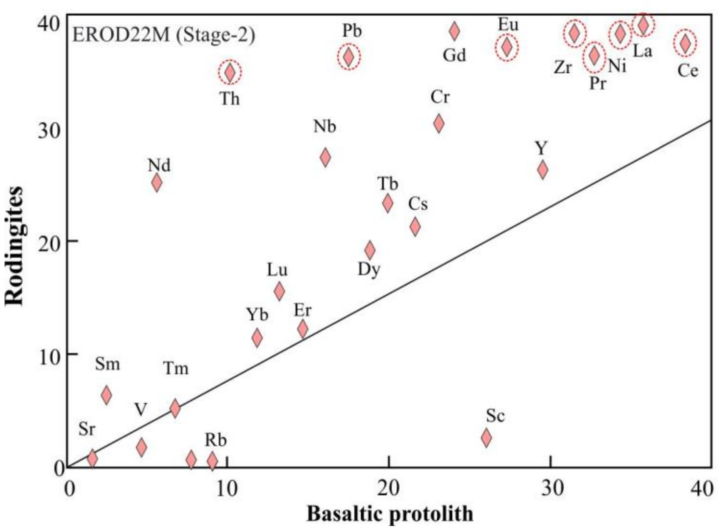
$Pl + Cpx + H_2O \rightleftarrows Hgrs + Chl + Di + Cm$ (2)

Formation of grossular (Salvioli-Mariani et al., 2020):

$Prh + Ca^{2+} + H_2O \rightleftarrows Grs + 2H+ + 0.5SiO_{2(aq)}$ (3)

Evolution of Metasomatism & element mobility





- **Stage-2:** Exhumation stage

- This stage is subdivided into two parts of increasing metasomatism. The second part is the mature stage of rodingitization and is characterized by the formation of distinct reaction zones with significant REE-enrichments.

- **Mineralogy:** This stage is characterized by the development of andradite, Mg-chlorite and vesuvianite.

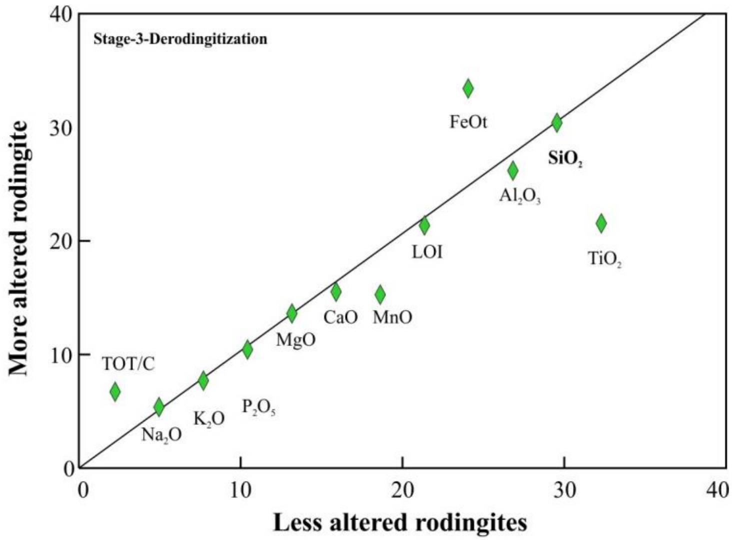
- **Element mobility:** Regarding Al as immobile, Ca, Mg and LOI were increased, whereas Si, Fe^t and total alkalis were depleted. REE including Y were **increased**.

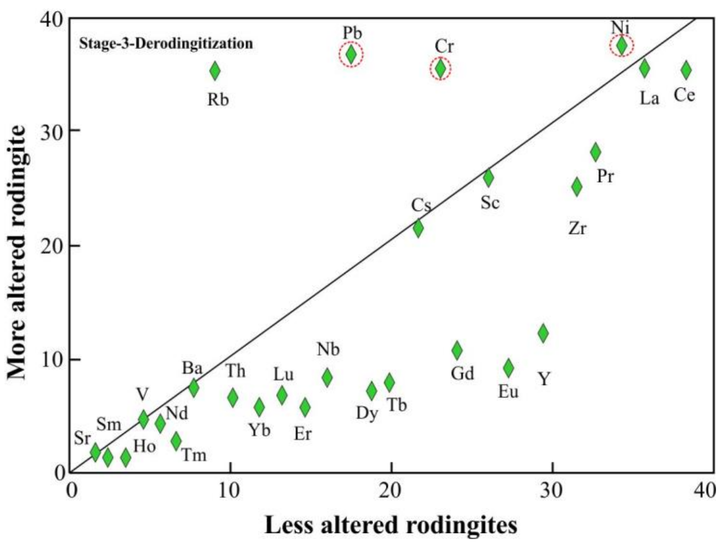
- **Mineral reactions:**

Formation of vesuvianite according to the following reaction proposed by Salvioli-Mariani et al. (2020):

$$5Grs + Di + Chl + 14Ca^{2+} + 7SiO_{2(aq)} + 16H_2O \rightleftarrows 3Ves + 28H^+ \quad (4)$$

Evolution of Metasomatism & element mobility





- **Stage-3:** Derodingitization stage
- Derodingitization resulted from the dissolution of the previously formed minerals (Stage-1 and -2). Derodingitization was in some cases accompanied by carbonation processes.
- **Mineralogy:** Chlorite was further increased, whereas calcite is usually one of the most common minerals.
- **Element mobility:** Regarding Si as immobile, Fe^t was increased, whereas Ca and LOI were depleted. REE including Y were depleted.
- **Mineral reactions:**

Formation of andradite is described by (Beard and Hopkinson, 2000):

$$\text{Grs} + \text{Cpx} + \text{Di} + H_2O \pm \text{Cm} \rightarrow \text{Adr} + \text{Chl} \qquad (5)$$

The reaction for calcite formation is described by Salvioli-Mariani et al. (2020):

$$\text{Grs} + 5\text{Di} + 4H_2O + 8CO_2 \rightleftarrows 8\ \text{Cal} + \text{Chl} + 10SiO_{2(aq)} \qquad (6)$$

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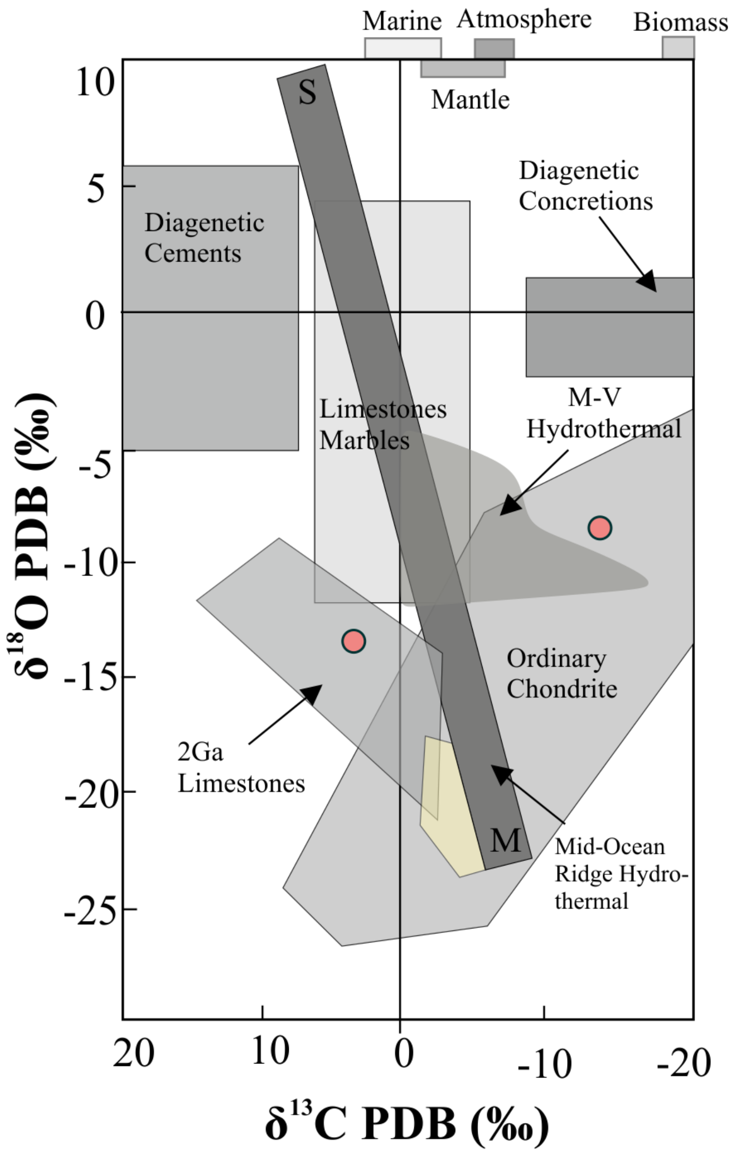
C-O isotopes



Isotope diagram modified after Rollinson, 1993

- **Fracture-filling calcite** was selected from **two rodingite** samples. These were analyzed for their δ^{18}O-δ^{13}C isotopic composition.
- The **small range** on their **δ^{18}O** composition is indicative of a common isotopic source that was probably associated with seawater fluids.
- The different δ^{13}C contents and more specifically the **negative δ^{13}C** values suggest **serpentinization-derived fluids** had significant contribution on the metasomatic processes.
- The aforementioned indicate that carbonation was a **complex phenomenon,** derived from **mixing processes** that involved the contribution of seawater and serpentinization-derived fluids.

Concluding remarks

1. Based upon their protoliths and REE composition, Central Evia rodingites are distinguished into **4 groups**.

2. Group-1: Rodingitization of Jurassic IAT-dolerites; **Group-2**: Rodingitization of Jurassic boninitic gabbroic protoliths; **Group-3**: Rodingitization of Triassic alkaline basalts and **Group-4** rodingitization of Triassic calc-alkaline subvolcanic rocks.

3. Metasomatic processes in Central Evia were developed in **three successive stages** of increasing metasomatic degree during the exhumation of mantle-wedge serpentinites.

4. Stage-1 represents the **initiation** of rodingitization, marked by the development of grossular, diopside and chlorite. This stage is substantially linked with serpentinization of the ultramafic host-rocks and the subsequent Ca-release due to clinopyroxene breakdown.

5. Stage-2 is the **main rodingitization** phase, which is characterized by the development of andradite, vesuvianite and Mg-rich chlorite. During this stage rodingites were significantly enriched in LREE. This **LREE-enrichment** was more profound at the marginal zones of Group-3 and Group-4 rodingites.

6. Stage-3 is linked with **derodingitization** processes. Chlorite and andradite tend to become the predominant mineral phases. Derodingitization was evolved under shallower depths with high Mg-fluxes. In some cases, **carbonation** processes were also developed as it is suggested by the occurrence of fracture-filling calcite. These processes mostly affected the rodingite marginal zones leading to remarkable **LREE-depletions**.

7. Stable isotope ^{13}C-^{18}O data from fracture-filling calcite of selected rodingite samples indicate a contribution of serpentinization-derived and seawater fluids during the development of carbonation processes.

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