PETROGEOCHEMICAL AND GEOCHRONOLOGICAL FRAMEWORK OF ELEMENT MOBILITY DURING MAGMATIC-METASOMATIC PROCESSES (CAMPIGLIA MARITTIMA, TUSCANY)

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Natural resources are a key issue for the society and their availability has been called into question (*e.g.*, Moss *et al.*, 2011). In this context, metasomatic rocks are one of the world's major source of Cu, Pb, Zn, Ag, Au as well as REE and HFSE. Metasomatism, which is defined as the process in which rocks change their composition while remaining effectively solid, is important in the evolution of a wide range of rock types, but it still remains quite poorly understood. Any crustal fluid can give rise to metasomatism when it migrates from one rock type to another. Metasomatism is usually related to existing pathway for fluid flow, such as fractures, faults, shear zones, or along lithological contacts. Processes of post-magmatic element mobilisation have been reported for a number of magmatic-hydrothermal systems occurring in various geodynamic contexts (Pirajno, 2013; Harlov & Austrheim, 2013). The determination of the constraints of the processes that control these types of systems is a challenging task because the effects of hydrothermal/metasomatic processes on element distribution are poorly know. Moreover, also the relationships of metasomatic processes and mineralisation stages have not been well documented, yet.

This study presents the results of a detailed petrogeochemical and geochronological investigation, involving mineral and bulk-rock analysis as well as a precise CA-ID-TIMS U-Pb zircon dating. Based on these data, a model has been developed to explain the role of metasomatic processes in mobilising elements in a granitic system and to define the timing of igneous events controlling the mobility of fluids observed at Campiglia Marittima (Tuscany, Italy) magmatic-hydrothermal system (Fig. 1).

The emplacement of the Botro ai Marmi pluton into the carbonate host rock produced *(i)* the thermal metamorphism of the host marble, later deformed in brittle regime, and *(ii)* a fracture system allowing metasomatic fluids circulation. The fluid-rock interaction promoted by circulation of hydrothermal fluids resulted in metasomatic processes and, thus, in the mobilisation of major (Fe, Ti, Si, Al, K, P) and trace elements (*e.g*. Th, Nb, Zr, HFSE, and REE), enriched in the hydrothermal minerals, mostly calc-silicates. These features are more marked close to the host rock contact and along fractures into the granitoid, with the occurrence of strongly zoned REE-rich minerals, as well as hydrothermal zircon and apatite. Detailed textural and geochemical investigations of the products of the hydrothermal activity (marble, exo- and endo-skarn, metasomatized granite) were carried out in the field as well as by means of optical microscopy, SEM-EDS, QEMSCAN, EPMA, and (LA)-ICP-MS. The aim of this work is to provide the timing of element mobility between granite, fluids and metasomatic bodies for a shallow crustal magmatic-hydrothermal system. In this context, the reconstruction of metasomatic processes, generating progressive elements mobilisation, asserts the importance of petrographic and geochemical characterisation of bulk-rock as well as major and accessory metasomatic minerals, for a correct petrogenetic interpretation.

Outline geometries and spatial relationship of the main geological bodies, mineralogical paragenesis and mineral zoning of a magmatic- hydrothermal system are important to reconstruct the timing of fluid-rock interaction and element mobility. Multiple metasomatic effects can overlap through time, resulting in complex mineral associations; moreover, a continuously renewed magmatic-hydrothermal system, with evolving fluid circuits, could produce several hydrothermal paragenesis (Fig. 2). The knowledge of the temporal relationships existing between metasomatic processes, mineral paragenesis, and element mobility, using textural, geochemical and accessory minerals dating technique, could provide a fundamental piece of information in order to identify potentially productive mineral deposits.

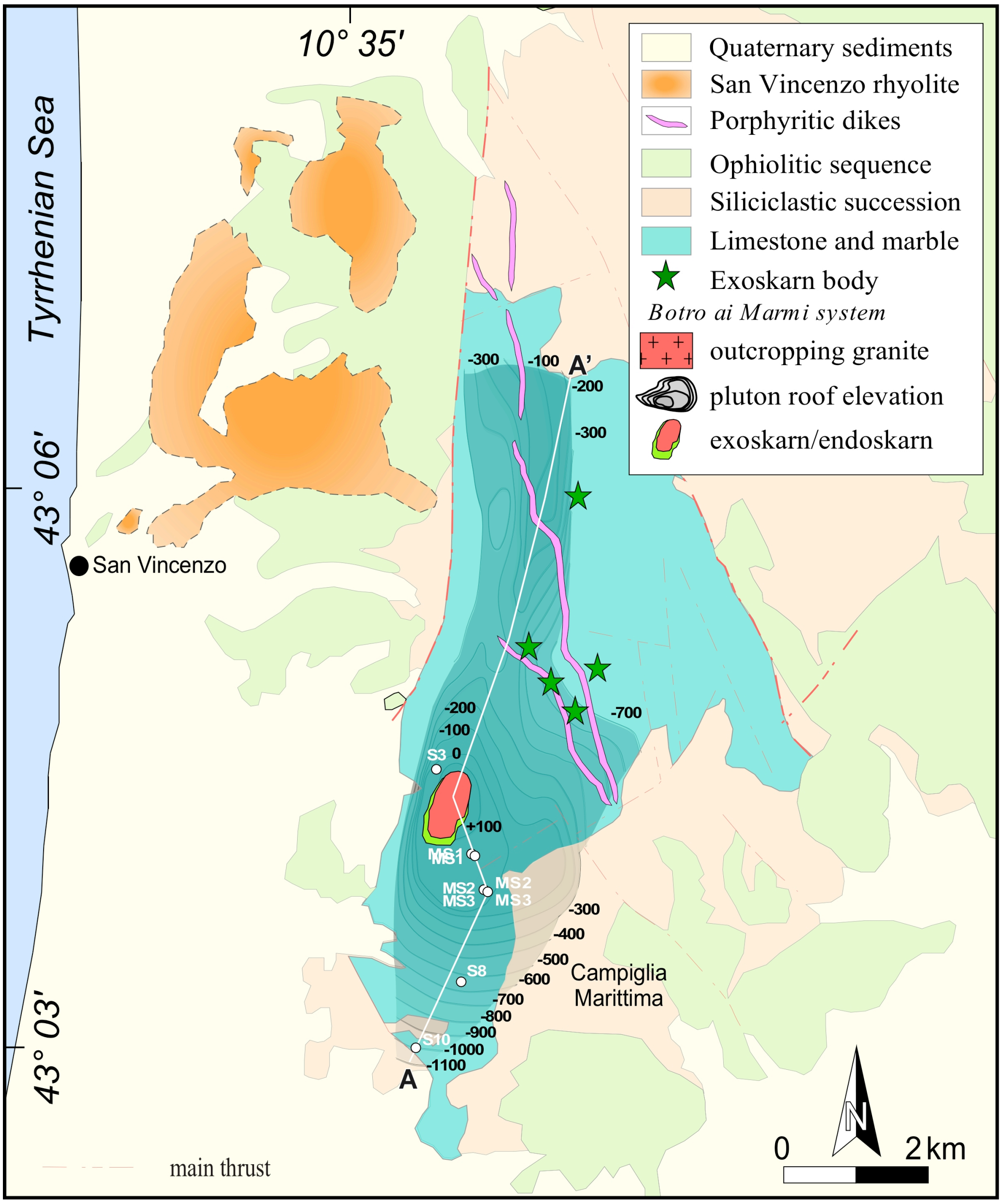

Fig. 1 - Schematic geological map of the Campiglia Marittima area, and interpretive map showing the pluton roof reconstructed by borehole log and geophysical data (modified after Vezzoni *et al*., 2017). Note the asymmetric pluton roof morphology with a maximum in the Botro ai Marmi outcrop. Furthermore, the host rocks show a strong thickness variation (progressively thicken away from the mine) and a strong thickness variation from southern to eastern side (Vezzoni *et al*., 2017).

Comparison of whole-rock chemistry of specimens is frequently used as an useful tool to trace the element mobility during metasomatic alteration. Indeed, it is necessary to know whether the constituents have really entered or have removed from the system. However, when certain components have been transported only locally, the comparison of whole-rock chemistry could hide some micro-scale processes (*i.e.*, replacement and pseudomorphism).

At "Botro ai Marmi" mineralogical, textural and geochemical investigation of granite, endoskarn and exoskarn bodies provided evidence for a potential contribution of Mg, K, Rb, Ba, Sr as well as gain of metals from an external source.

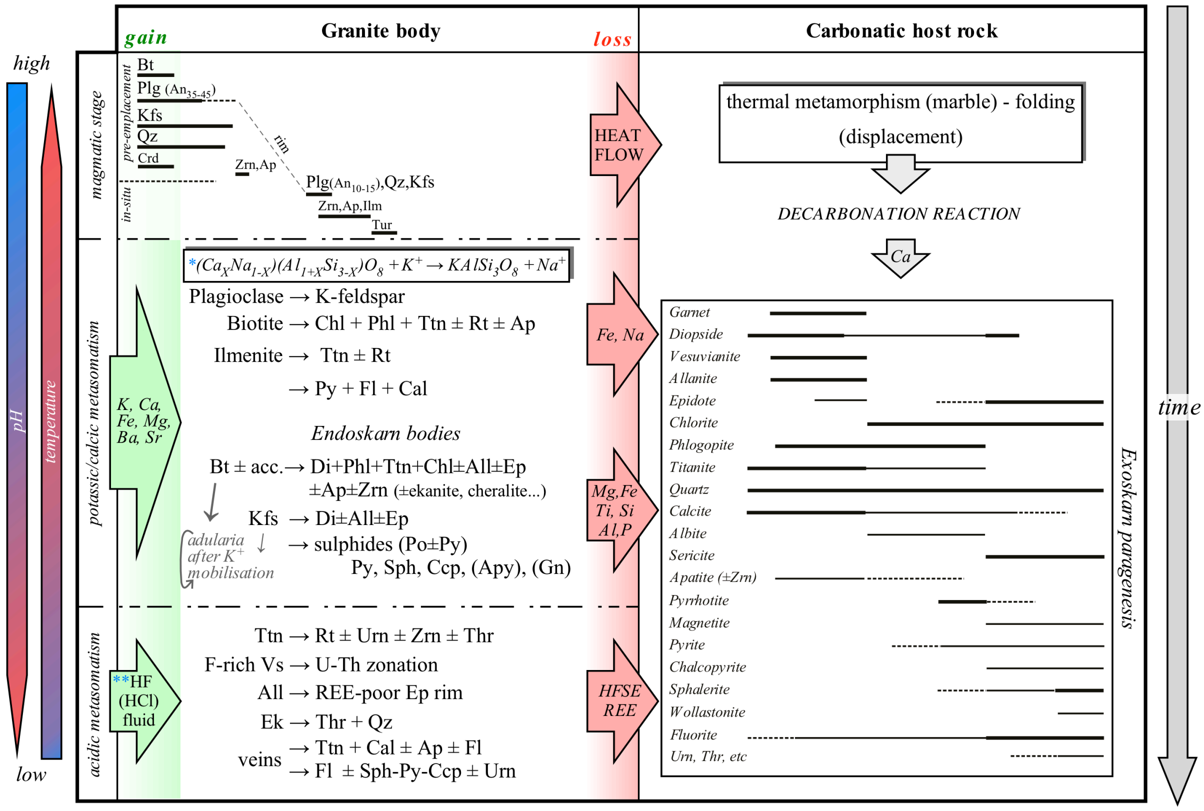

Fig. 2 - Mineral paragenesis summarising the original and metasomatic mineralogy from the granite body and the carbonate host rock. *Plg rim (An10-15) completely replaced by Kfs, while Plg core (An35-45) partially replaced. **calc-silicates dissolution/replacement, HFSE and REE local mobilisation, chemical zoning (*i.e.*, Vs, Ttn, Di, Grt); mineral abbreviation according to Whitney & Evans (2010).

The metasomatic activity can be subdivided into a potassic/calcic metasomatism, and a lower temperature acidic metasomatism (Fig. 3). Initially, a potassic/calcic metasomatic event led to the complete metasomatism of magmatic biotite, plagioclase, and ilmenite, promoting major element mobilisation (Fe, Na, P, Ti) and crystallisation of K-feldspar, phlogopite, chlorite, titanite, and rutile. Significant gain of Mg, K, Rb, Ba and Sr were accompanied by loss of Fe and Na. Metals (*i.e.*, Cu, Zn, Sn, W, Tl) showed a significant mobility during metasomatism. The increasing fluids acidity due to increasing Ca-activity resulted in a diffuse Ca-metasomatism (Fig. 3). During this stage occurred a wide variety of calc-silicates (*e.g.*, diopside, titanite, vesuvianite, garnet, epidote), particularly abundant at the carbonate-granite contact and along joints into the granite.

Upon cooling, fluids became more acidic and fluorine activity increased, with the widespread crystallisation of fluorite, corresponding to the textural disequilibrium of former calc-silicates. Ca-F-rich fluids enhanced the acidic metasomatism of accessory minerals and the mobilisation of HFSE and REE. This stage was characterised by the exchange of major elements (Ti, Ca, Fe, Al) with HFSE and REE in the forming metasomatic minerals (*i.e.*, titanite, vesuvianite), and the crystallisation of HFSE-REE minerals. Moreover, the common textural disequilibrium of newly formed minerals (pseudomorphs, patchy zoning, dissolution/precipitation textures) testifies the evolution of metasomatising fluids toward more acidic condition (Fig. 3). Concluding, the selective mobilisation of such components was related to a change in fluid composition, pH and temperature.

This study emphasises the importance of relating field studies to petrographic observation and detailed geochemical analysis. Moreover, it shows how such linkage can lead to the construction of litho-geochemical model for element mobilisation in crustal magmatic-hydrothermal setting.

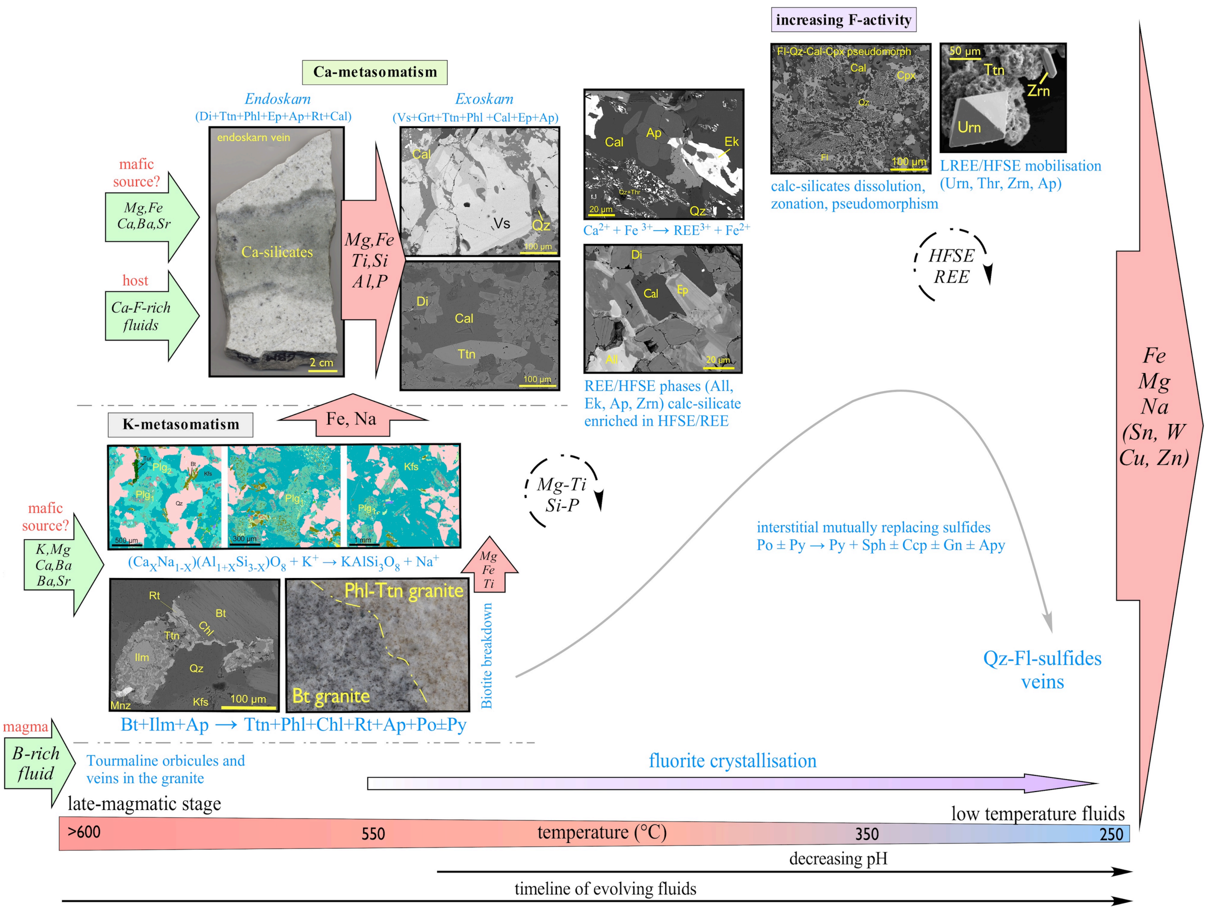

Fig. 3 - Schematic model for the progressive element mobility observed at the "Botro ai Marmi" metasomatic system. The diagrams define the main mechanism responsible for the selective mobilisation of elements indicating the possible litho-geochemical vectors for the metasomatic processes.

The Campiglia system offers exposures of the full range of emplacement types for magmas and related fluids, thus representing a prime case study to investigate the timescales of mechanism of magma deep storage, extraction, transfer, and shallow emplacement/eruption. New U-Pb CA-ID-TIMS geochronology from the Campiglia igneous system allows to reconstruct the evolution of crustal-derived and mantle-derived magmas that fed plutonic, subvolcanic and volcanic units over 1000 ka (Fig. 4).

Distribution of zircon ages is at odds with what can be expected for the crystallisation interval of an igneous body. Indeed, that interval is short for the "Botro ai Marmi" pluton (100 ka), intermediate for the subvolcanic mafic Temperino porphyry (450 ka), and long for the volcanic San Vincenzo rhyolite (700 ka). The youngest zircons from the Botro ai Marmi granite have ages identical to ^{40}Ar-^{39}Ar ages of biotite from the granite and metasomatic phlogopite from skarn crosscutting the granite.

The Temperino mafic porphyry and the San Vincenzo rhyolite show younger sanidine ages (emplacement/eruption age). The youngest zircon age from the pluton is therefore assumed to approximate the age of emplacement and final crystallisation of the melt, whereas the zircons from the Temperino mafic porphyry and the San Vincenzo rhyolite are considered antecrystic, derived from re-mobilised earlier magma extracted from a deeper reservoir at the emplacement age.

The new documentation of an extended period of crystallisation for the Campiglia igneous system (~1000 ka) matches with observations for the long-lived magmatic systems of Larderello and Elba Island (Barboni & Schoene, 2014; Caricchi *et al.*, 2016). Geochronological data for the Campiglia igneous system lend support to a scenario where a bimodal deep reservoir remains in a magmatic condition (melt-present) for ~1 Ma.

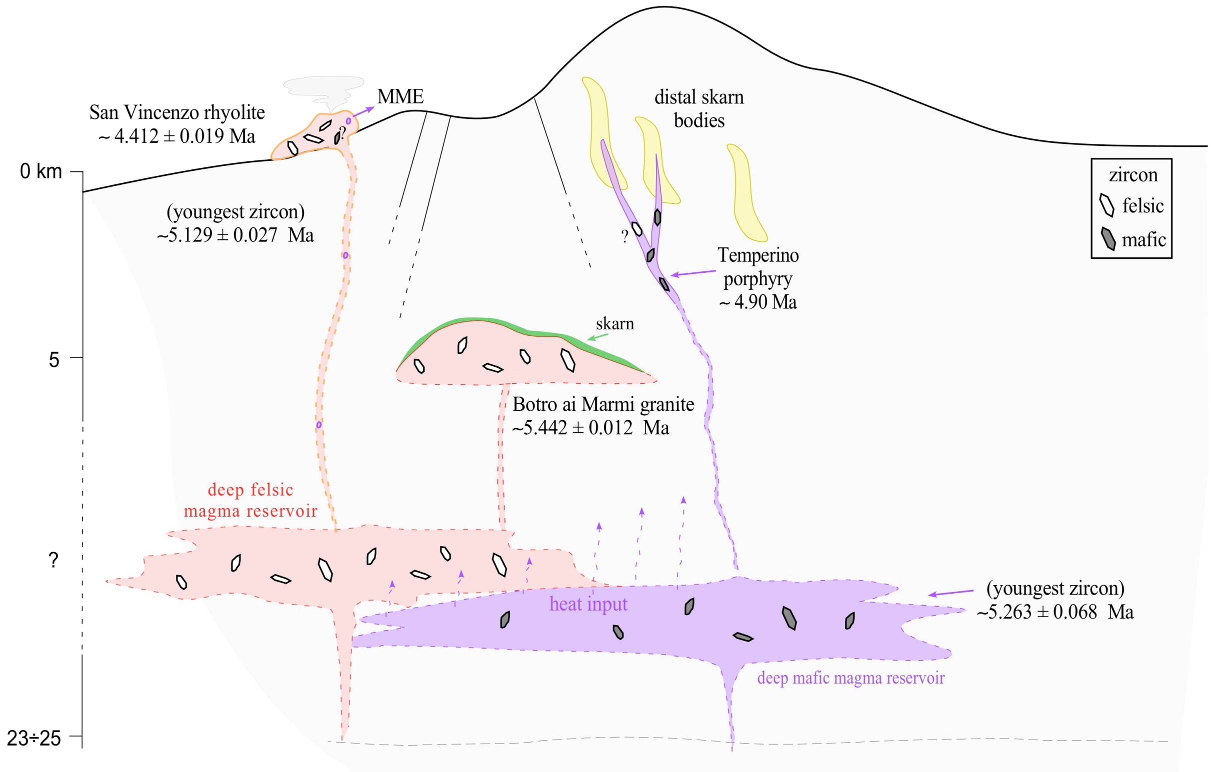

Fig. 4 - Schematic model for the evolution of the Campiglia Marittima magmatic-hydrothermal system, not to scale. Between bracket is indicated the emplacement/eruption age.

The magma extraction from a crustal felsic reservoir fed a pluton and its hydrothermal system during a short time interval at 5.4 Ma. At ~4.9 Ma the extraction of magma from a mafic reservoir fed the Temperino mafic porphyry. Finally, the late extraction of magma from the felsic reservoir (probably the same of the Botro ai Marmi granite) fed the San Vincenzo rhyolites, where early-crystallized zircons were transported/recycled within portions of melts extracted from the reservoir.

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