New considerations on trace elements for quarry provenance investigation of ancient white marbles

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ABSTRACT

Geochemical data on fine-grained white marble from Carrara (Italy) and Göktepe (Turkey) obtained using *in situ* Laser Ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) suggest that the application of this technique for trace elements determination is a promising method for provenance investigations. The REEs patterns of Carrara samples are similar for almost all quarries, even if they differ in the absolute concentrations; whereas samples of Göktepe have lower concentrations and different patterns of REEs than those of Carrara, thus contributing to solve provenance attribution. In addition, statistical treatment of data by means of principal component analysis (PCA) discriminates clearly Carrara quarries from those of Göktepe.

1. INTRODUCTION

Marble material was widely used for artistic, sculptural and architectural artifacts over the history of Mediterranean world (Attanasio *et al.*, 2006). The investigation of the ancient exchange systems is a major topic of archaeological research, aiming to understand economic aspects and political systems of ancient societies and to identify the sourcing area of the raw materials used for artistic purpose.

In addition, scientific studies can contribute to the identification of copies forgeries and restorations as necessary pre-requisites in the planning of conservation and restoration (Attanasio, 2003).

In the last centuries, studies on white marble were of great interest, leading researchers of different disciplines to provide information for the identification of the quarrying area by means of macro and micro observations.

The first attempt dates back at the end of the XIX century, when Lepsius used the optical transmission microscope to assign the provenance of several important archaic sculptures in Athens, with appreciable confidence (Lepsius, 1890). This was the only method utilized for many years and it remains important today.

During the first half of the twentieth century, the use of optical microscopy was gradually accompanied by chemical techniques (XRF, OES, AAS, INAA) for trace elements determination, (Herz and Garrison, 1998, Meloni *et al.*, 1995; Zöldföldi *et al.*, 2008; Matthews, 1997; Green *et al.*, 2002; Moens *et al,* 1988; Roos *et al.*, 1988; Asgari and Matthews 1995; Lapuente, 1995). Since 1970 the determination of stable isotope concentrations were proposed as the most powerful technique among others (Craig and Craig, 1972). In the literature are reported many studies based on mineralogical-petrographic and C-O stable isotopic data (e.g., Manfra *et al.*, 1975; Lazzarini *et al.*, 1980a; Herz, 1987,1988; Herz and Dean, 1986; Moens *et al.*, 1992; Gorgoni *et al.*, 2002; Capedri *et al.*, 2004), others deal with electron paramagnetic resonance data (EPR), stable isotopes and certain petrographic parameters such as the maximum grain size (MGS) (e.g., Attanasio *et al.*, 2000, 2006; Polikreti and Maniatis, 2002). In addition, the results of cathodoluminescence microscopy, combined with stable isotopes have been used for known classical quarrying areas (e.g., Barbin *et al.*, 1989, 1991; Lapuente *et al.*, 2000).

During the last two-century, the main problems dedicated to the provenance studies of white marble are principally two. First of all, the growing number of new data and the frequent cases of overlapping phenomenon among quarries, through located in different basins of Mediterranean areas, generated a more confused frame for the large amount of database on marble compositions. The second issue was due to the heterogeneity of materials, also within the same mining district, where the concentrations of the trace elements (in the range of ppm) are often below the detection limits of the traditional techniques. These drawbacks did not permit accurate and reliable results, which negatively affected? provenance studies of a given marble, based on trace elements.

Recently, different studies point out that the combination of databases with mineralogical, chemical and physical parameters can help to discriminate among ancient quarries (Lapuente *et al.*, 2014). A single analytical technique did not prove to be conclusive, and multi-analitycal methods, using sequentially or simultaneously variables from different techniques, are currently considered the only possible approach for provenance studies (Lazzarini, 2004; Attanasio *et al.*, 2006; Antonelli & Lazzarini, 2015).

Ebert **et al. (2010)** suggest that concentrations of trace elements (especially rare earths) by means of LA-ICP-MS in calcite marble from different sites of the island of Naxos, were useful to discriminate among different quarries. This technique thanks to the detection limits, even lower than the concentrations of the trace elements, has made possible the acquisition of analytical data essential to discriminate marbles from different mining sites and within the same site.

Afterwards, the study published in 2013 on Turkish white marble from Göktepe highlighted a new problem (Attanasio *et al.*, 2013). Although isotopic values and petrographic features are homogeneous within Goktepe districts, these results are often very similar to those shown by Carrara and Docimium marbles. These authors state that the most relevant feature of Göktepe marble is the high strontium and low manganese concentrations, suggesting for the future work the possibility to measure the concentration of additional trace elements.

The present work aims to compare ? the Carrara and Goktepe marbles, which are very similar for petrographic and isotopic fingerprints and never discriminated until now through analytical methods cited above.

Here are reported and discussed the results of *in situ* LA-ICP-MS technique, whose application permit the discrimination of these two famous white marble from Italy and Turkey.

2. ARCHAEOLOGICAL PROBLEM

The growing interest for Goktepe white marble in archaeometric field is a relative recent issues as the quarries were discovered by Yavuz in the 1996 and discussed only in the 2006 (Yavuz et al., 2009).

Until then statues and artifacts with features close to this marble were attribute to Carrara or Docimiun ones. The discovery of the Goktepe quarrying site appear immediately interesting for two reasons, *i.e.*, the high quality of this marble, testified also by the numerous traces of extracting activity, and the proximity to the Aphrodisias site. This suggested immediately a possible prominent role in the history and tradition of the exploitation of fine-grained Goktepe marble (Attanasio *et al.*, 2013).

A systematic characterization of this litotype, compared with other geological white marbles from important ancient quarries and archaeological artifacts, opens a new topic in provenance investigation of Mediterranean fine-grained white marbles.

The initial studies, *i.e.,* petrographic and isotopic signatures, confirmed the analogies among Goktepe, Carrara and Docimium marbles. In this context, the discovered of the new quarrying sites in Goktepe region and the growing interest for geochemical techniques, require a deep investigation to find proper geochemical markers useful to discriminate among these similar marbles.

3. GEOLOGICAL SETTING

Carrara white marble, quarried from the Apuan Alps, is formed during a regional metamorphic event and developed under greenschist facies conditions of originally carbonatic rocks, deposited in a shelf environment during Rhaetian-Liassic times (Cantisani *et al.*, 2005). The marbles are part of the lower to middle Liassic carbonate platform sequence of the former Apulian continental margin, which was deformed and metamorphosed during the Apennine orogeny (Oesterling *et al.*, 2007).

The Apuan marbles are involved in the main tectono-metamorphic events that interested the Massa and Apuane units. From the Upper Oligocene, after the closure of the Tuscan sedimentary sequence with the deposition of Pseudomacigno sandstones, two main polyphase tectono-metamorphic events can be recognized, *i.e*., the main deformation event (D1) has started in Late Oligocene times as part of a crustal shortening regime (dated with the K/Ar and the ^{40}Ar/^{39}Ar methods at 27 Ma byGiglia and Radicati di Brozolo, 1970; Kligfield *et al.*, 1986). It gave rise to kilometer-scale isoclinal folds, antiformal stack development and shear zones formation. The second event D2 begun in the Early Miocene (12-14 Ma) as the result of crustal extension, dated at 10-8 Ma (Kligfield *et al.*, 1986) deforms all earlier structures, developing folds and shear zones (Carmignani *et al.*, 1980; Carmignani and Kligfield, 1990; Molli *et al.*, 2000).

Since pre-Roman age, Carrara white marble from Alpi Apuane were extensively exploited in four quarries, located in two different districts , *i.e.,* Gioia, Fossacava, Calagio from Colonnata district and Sponda I from Torano district, respectively (Fig.1).

Turkey is subdivided geologically into three main tectonic units and Goktepe white marble is quarried from Anatolides-Taurides unit, that is subdivided into zones with different metamorphic features, as suggests by

Ketin (1966). Goktepe quarrying sites are located in the Menderes Massif, an extensional metamorphic core complex, in the western Anatolian extensional province.

To the northwest of Menderes Massif there is a belt of chaotically deformed uppermost Cretaceous-Palaeocene flysch with Triassic to Cretaceous limestone blocks. At the basement, it contains successions of regionally metamorphosed rocks consisting of gneiss, mica schist and marble beds.

Stratigraphically, the upper part of the Menderes Massif's cover series is represented by a platform succession of detrital and carbonate rocks. The platform-type marble successions range in age from Triassic to Late Cretaceous, and are overlaid by a red pelagic marble horizon and flysch-type detrital rocks of Late Cretaceous to earliest Eocene age (Güngör and Erdogan 2002). In the Muğla area of south-west Turkey, the marble beds are generally found as long lenses within the cover series in the southern flank of the Menderes Massif metamorphic rocks (Yavuz *et al.,* 2005a,b) (Fig. 1b).

The samples studied here come from quarries located in the province of Muğla, approximately 30 Km north east of the provincial capital and 40 Km southwest of the ancient city of Aphrodisias (Attanasio *et al.*, 2013).

4. EXPERIMENTAL

Materials

In this work 31 geological sample of white marble from Carrara (19) and Goktepe (12) were studied using LA-ICP-MS with the aim to identify among trace elements important geochemical markers useful to discriminate these two marbles.

Sampling was made considering the overall geological unit volume, the different quarrying faces and its variability, and the quarrying activity in the history of the two localities.

The 19 specimens of Carrara white marble were sampled in four quarries, located in two different basins on the western slopes of Monte Sagro, near Carrara city, *i.e.,* Gioia, Fossacava, Calagio (Colonnata district) and Sponda I (Torano district); whereas the twelve specimens from Goktepe were sampled in ancient quarries of the province of Muğla.

Methods

A geochemical characterization of white marble samples was performed by means of Laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS).

Analyses have been carried out at Laboratory of Inorganic Chemistry of Eidgenössische Technische Hochschule (ETH) of Zurich and at CNR-Istituto di Geoscienze e Georisorse, U.O.S. of Pavia.

The two analytical instruments present a different general set-up.

The LA-ICP-MS system at ETH of Zurich (Department of Chemistry and Applied Biosciences Laboratory of Inorganic Chemistry), consists of pulsed 193 nm Excimer laser from Lambda Physik with an energy-homogenized GeoLas optical system, coupled with a Perkin Elmer Elan 6100 DRC, and ICP quadrupole mass spectrometer.

The laser energy applied on the sample was 12 J cm^{-2}, the laser frequency was 10 Hz and the ablation aerosols were carried to the ICPMS by He-Ar gas. The laser spot was 80 µm craters. External standardization was made using the standard reference glass NIST 610 and CaO was used as internal standard.

The lower limits of detection vary for the measured elements over a range of two or three orders of magnitude (10^{-1} to 10^{2} µg g^{-1}), and the LODs are controlled by a laser with 10 Hz repetition rate.

The system at CNR-Istituto di Geoscienze e Georisorse, U.O.S. of Pavia consists of 266 nm Nd:YAG laser source (Brilliant, Quantel) coupled with a Perkin Elmer DRCe system, and a ICP quadrupole mass spectrometer. The laser was operated at 10 Hz with pulse energy of about 35 mJ, and a spot size of 60-80 µm. The NIST SRM 610 was used as the external calibration standard, and CaO was used as the internal standard for calcite.

In both laboratories were performed 5-7 measurements for each sample, depending on chemical variation in the sample.

5. RESULTS

Table 2 summarizes the concentrations of the trace elements measured using the laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) in white marbles from Goktepe and Carrara. Single calcite crystals were analyzed for trace and rare elements, for a total of fifty-one elements. Bisognerà scrivere una didascalia per la tabella spiegando che I dati sono tutti riportati in ppm. Questi sono I valori di Zurigo, Pavia o una media? Bisognerebbe anche sostituire la virgola (,) con il punto (.)

Part of these has been presented by multi elemental diagram, so called spider diagram, where the systematic variation in trace elements is illustrated by plotting the log of their relative abundances, which are calculated by dividing the concentration of each trace element by its concentration in a set of normalizing values such as those of chondritic meteorites. Trace element concentrations have been normalized to common reference standard chondrite values given by Sun and McDonough (1989).

In figure 2 the concentrations of the large-ion litophile (LIL), the high-field strength (HFS), and the rare earth elements (REE), plus Y of Carrara and Goktepe marbles are reported in the chondrite normalized multi-element diagram.

The LIL elements of Carrara districts marbles, *i.e.*, Colonnata and Torano, display enrichment in Ba and in Sr, whereas the concentrations of Rb and K are scattered. On the contrary, Rb, Ba, and K have a variable content in Goktepe marble, those partially fall in the range of Carrara marble or quite low, even though Rb and K are significantly scattered. Sr content for Goktepe samples is higher and displays a wide range of concentrations respect to those of Carrara. The marked separation between the two quarrying sites is highlighted in the diagram Sr content *vs* sum of LILE (Cs, K, Pb, Eu, Na, including Sr), where Carrara specimens form a narrow cluster separated to those of Goktepe (Fig 3).

The patterns of HFS element distribution are very similar for all Carrara samples, having enrichment in U, Ta and Hf and depletetion in Th, Nb, Zr and Ti. However, the absolute concentrations are variable; in this regard the concentration of Hf seems to discriminate the quarries of Fossacava (rhombus symbols) and Calagio (circle symbols) that have the lowest content, and Sponda I (triangle symbol), which has intermediate values and Gioia (square symbols) that displays the highest content. (Fig. 2)

The HFSE patterns of Goktepe marble are quite similar to those of Carrara, with a depletion in Th, Nb, Zr, Ti, an enrichment in U and Nb and, to some extent in Hf. Titanium and, even more, zirconium display low concentration, except for few samples.

Among the trace elements, the REEs are the group (fig. 2) that had better discriminate marbles from the two different ancient quarrying areas. These REEs concentrations of Goktepe are significantly lower than

Carrara. A marked negative anomaly of Ce and the low concentration of Y further discriminate between the two sites.

Observing the spider diagram, HFSE and REEs have different absolute concentrations among the specimens and in fig. 3 the REEs plus Y *vs* HFSE (Sc, Th, U, Pb, Zr, Ce, Hf, Ti) diagram shows a good level of discrimination between the two districts. Goktepe samples form a separate cluster from those of Carrara, having the lowest content of HFSE and REEs+Y.

6. DISCUSSION

Among different analytical techniques, the LA–ICP–MS is particularly valuable for trace elements characterization of stones of archeological interest as it combines the capacity of analyzing a great number of trace elements with micro-destructivity and high sensitivity, in a very short time, features that make it a very powerful tool for provenance determination of white marble.

For more than a century, the scientific community applied several analytical techniques to determine the provenance of white marble, widely used in the field of cultural heritage. One of the main topics is related to the similar petrological and chemical features that characterized these marbles.

In particular, the recent discovery of the ancient marble quarries of Goktepe site opened up a new debate on the characterization of the site. Goktepe marble has geochemical and petrographic features and stable isotope values similar to those of Carrara, and it is not possible to solve the issue so far.

An exhaustive study on white sculptures from Hadrian's villa examines in depth these two white marble using petrographic observations, cathodoluminescence, stable isotope and EPR. Even though unambiguous petrographic features between Göktepe and Carrara came out quite clearly, as the average fine grain, the provenance attribution seemed to be uncertain when the data are compared with the available databases on fine-grained white marble (Lapuente *et al*., 2012a, 2012b).

A part from the grain size, Carrara and Goktepe are quite similar petrographically, with textures ranging from homeoblastic to partially heteroblastic. Despite of the finest grain of Goktepe, it often exhibits the presence of coarse calcite crystals and the MGS value is not very different from the value measured for other fine-grained marbles and has a discriminant power that is lower than expected (crf. Tab 1).

Oxygen and carbon isotopes revealed controversial results in discriminating marbles of different provenance; however, they remain the most used parameters for this type of study.

In the present study the isotopic values of the samples are very homogeneous and quite indicative of the Göktepe provenance, although not much different from Carrara samples. The average values of $\delta^{18}O$ and $\delta^{13}C$ for Carrara are -1.7; 2.03 (Gioia), -1.6; 2.1 (Fossacava), -1.0; 1.9 (Calagio), -1.76; 2.16 (Torano), and for Goktepe -2.9; 2.6, respectively. However, even if these date are different, when are considered all fine-grained marbles from Mediterranean area a series of overlapping exists (Attanasio *et al.*, 2006).

A recent study reported the concentrations of a limited numbers of trace elements mainly, *i.e.*, Fe, Mn, and Sr, substituting Ca in the structure, with concentrations in the range of 10-1000 ppm (Attanasio *et al.*, 2013). These elements have been used to characterize Goktepe marble and to compare these data with other white marble deposits from Mediterranean basin, aiming to provenance attribution.

Furthermore, considering all drawbacks, *i.e.*, overlapping of the data and similar petrographic and geochemical features of different fine-grained marble, some authors consider important the use of multi-analytical approaches, aiming to provenance attribution of white marble.

The successful application of the LA-ICP-MS for the geochemical characterization of the Naxos white marble (Ebert *et al.*, 2010), opened a new possibility to discriminate the two white fine-grained marble of Goktepe and Carrara.

In our study case, the application of LA–ICP–MS allowed to measure the concentrations of more trace elements (51) than before, with absolute concentrations often too low to be detected with the methodologies currently used in archaeometric field.

The novelty of this study consists in the possibility to investigate other fingerprints (*e.g.*, REEs) to characterize the two quarrying sites and within the districts of these.

Among trace elements, the contents of the REE (+Y) and other elements (*e.g.*, Mn, Sr, Pb, Zr, Ti) seems to be the better geochemical markers to characterize the marble from Goktepe district. In particular, their e concentrations are sometimes below 0.01 ppm, exclusively detectable using LA-ICP-MS.

The multi-elemental diagram points out the most characterizing trace elements (*e.g*, LILE, HFSE, REEs + Y) between the two quarrying sites of Carrara and Goktepe for absolute concentrations and patterns of distribution. Although these groups of traces resulted helpful for the provenance discrimination, we consider also other trace elements such as Fe, Mn and Sr. The selection of these elements is based on the elements considered in the previous studios in many cases, or elements never observed so far because below of the detection limit of the most of the analytical techniques.

The diagrams in figure 3 and 5, *i.e.*, Sr *vs* sum LILE and Fe+Mn *vs* sum REEs highlighted that the samples from Carrara and Goktepe provenances fall into separate clusters broadly distinct, confirming what observed by Attansio *et al.*, 2013. Goktepe specimens have higher content of Sr ranging from 428 to 836 ppm respect to Carrara marble, which range between, whereas Carrara samples have higher content of Mn (11-51 ppm) compared to Goktepe (0.8-3 ppm), usually one or more order of magnitude.

The HFSE (fig.4) content in Goktepe marble range from 0.4 to 1 ppm, whereas for Carrara sample their content varies from 1.4-32 ppm, which further discriminates between the two Mediterranean basins.

In detail, Carrara samples show different concentrations of HFSE, especially for Sponda I sample that has a high content of Pb (2.4 ppm) that could derive from hydrothermal fluid exsolved during formation of the rocks. The content of Ti and Zr in Goktepe samples is constantly below 0.2 ppm, whereas for samples of Carrara Ti is in the range 0.3-25 ppm and Zr from 0.03-1.6 ppm.

The REE elements are the most powerful markers to distinguish the two sites and observing the sum of these elements some considerations come out. In detail, the sum of the REEs is 0.8-4 ppm for marble of Colonnata district and 9 ppm for Torano district, whereas for Goktepe is between 0.1 to 0.3 ppm. The negative anomaly of Ce and the low concentration of Y contribute to distinguish between Goktepe and Carrara marble. Goktepe samples are characterized by a sharp negative Ce anomaly compared to Carrara, confirmed by the Ce* values. The anomalies were quantified by comparing the measured concentration with an expected concentration, obtained interpolating the normalized values of the elements La and Pr for Ce* and Sm and Gd for Eu*, according to the formula $Ce^* = \sqrt{LaN \times PrN}$ and $Eu^* = \sqrt{SmN \times GdN}$, where N=chondrite normalized, recommended by Taylor and McLennan (1985).

Carrara has a negative anomaly for Ce, with an average value for Colonnata of 0.5 (for all the quarries) and for Sponda I of 0.6. Instead the Eu anomaly has Eu*N values different not only for the two districts but also within Colonnata district, having 1.6 value Gioia and 1.3 Fossacava, respectively. Goktepe has negative Ce anomaly with Ce* values from 0.3 to 0.6. The different behaviors of Ce probably reflect the variable oxygen fugacity conditions during calcite growth because this element have a multiple oxidation states (Ce^{3+}, Ce^{4+}) under geological conditions (Ebert *at al.*, 2010).

The most characterizing trace elements of the two districts are shown in fig. 6a, where the absolute concentrations in Goktepe specimens are the lowest. The content in Mn, Pb, Zr, Ti, Ce, Y, and the sum of the REEs are an order of magnitude lower than in Carrara, that has an enrichment of all these trace elements, except in Sr. In addition, these elements have been treated with statistical method PCA and fall in two separate clusters thanks to different concentration of geochemical markers.

7. CONCLUSION

Thirty-one samples of white marble from ancient Carrara (Italy) and Goktepe (Turkey) quarries have been studied, aiming to quantify trace elements for provenance purpose by using LA-ICP-MS.

In particular, the concentration of the REEs, often in the range of the detection limits for the majority of the analytical techniques employed in archaeometric studies, identified as geochemical markers and characterizing of the variability of Carrara and Goktepe quarrying districts. Indeed, Goktepe marble is characterized by very low content of REEs, lower than 1 ppm. On the contrary, the REEs content in Carrara samples is higher and the patterns are different compared to those Goktepe samples, thus resulting useful to differentiate the samples of these two areas.

The data set might spread the field of provenance if the sample area will be expanded, especially in the case of Carrara marble, where the variability within the districts has been observed. Since trace elements seem to be promising to characterize the fine-grained white marbles, it is necessary to implement the number and the extraction sites of the samples to build a larger database with all the geochemical information, correlate with minero-petrographic features. Our preliminary data highlight that the contribution of trace elements and in particular that of REEs, may help to solve the intriguing archaeological problem of attribution of white fine-grained marble, and seem particularly indicate when too analogies exist as in the case study between Goktepe and Carrara marble.

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Fig. 1. Map showing the geographical locations of the quarries sampled for this study.

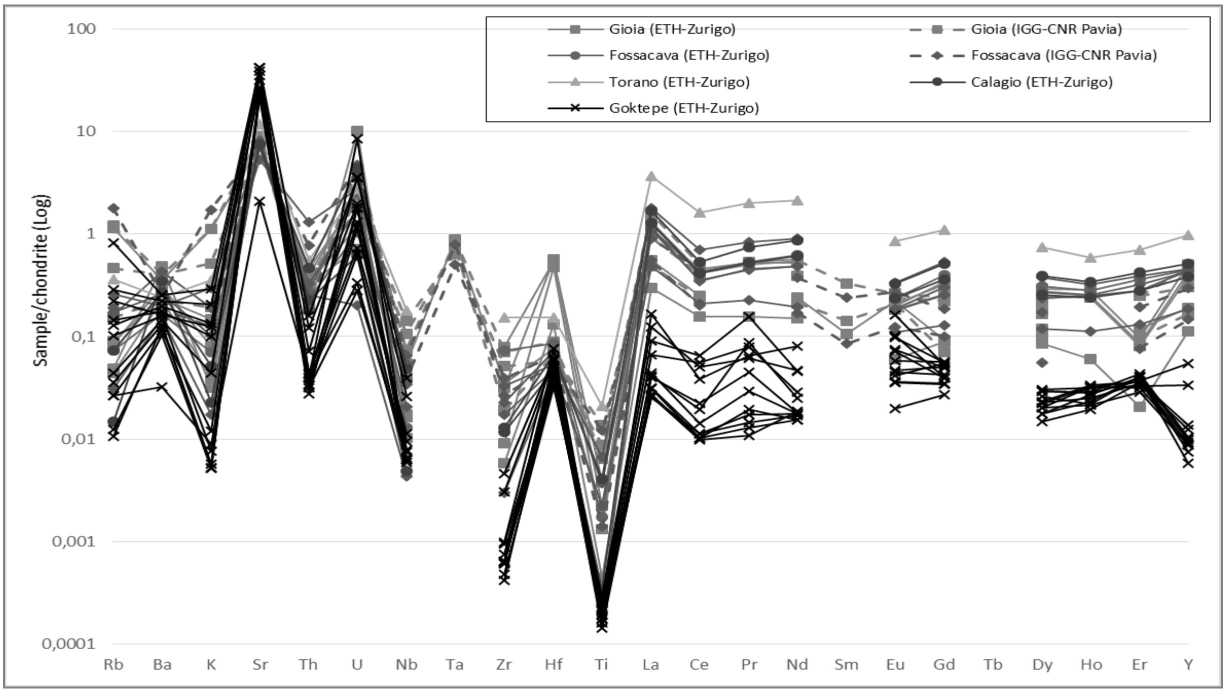

Fig. 2: Distribution of trace elements in calcite are given for white Carrara (Italy). The two districts are displayed using differing symbols and colors: line with square symbol for Gioia quarry, line with rhombus symbol for Fossacava quarry, line with circle symbol for Calagio quarry and line with triangle symbol for Sponda I. Goktepe samples are displayed using black line with cross symbol. Moreover, continuos lines are for samples analyzed at the ETH of Zürich, while dash lines for those analyzed at the IGC-CNR Pavia. The concentrations are normalized to chondrite (Sun and McDonough (1989)).

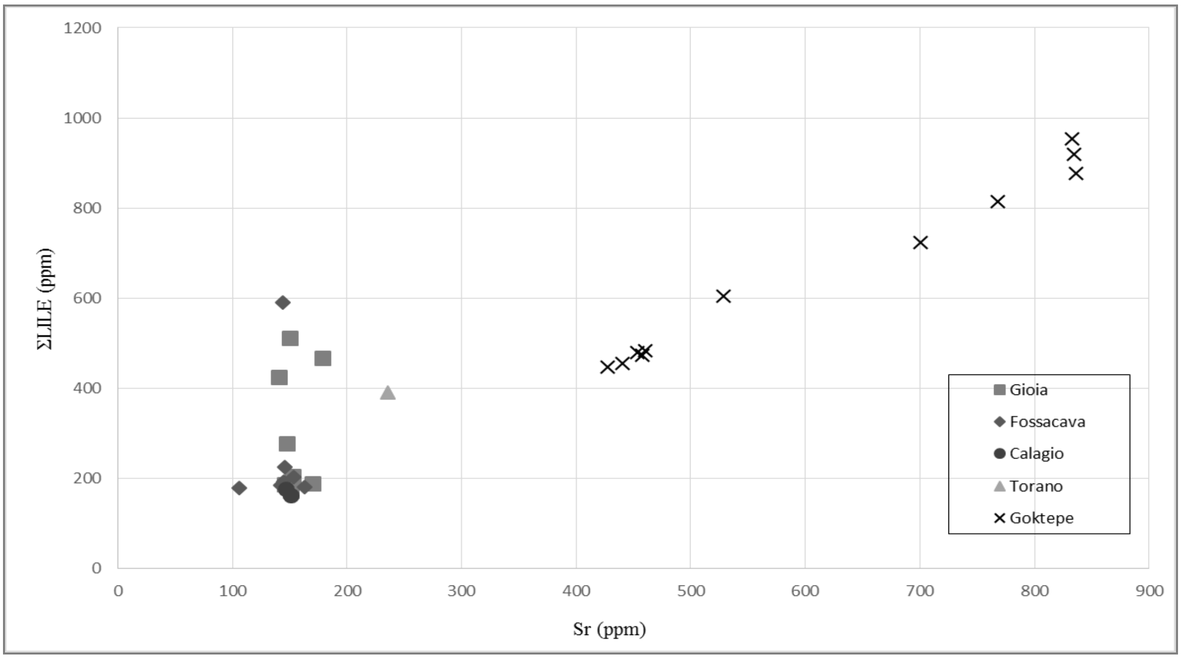

Fig. 3: Sr vs LILE content in Carrara and Goktepe samples. The two quarrying sites fall into separate clusters broadly distinct. Goktepe specimens have a higher content in Sr, ranging from 428 to 836 ppm.

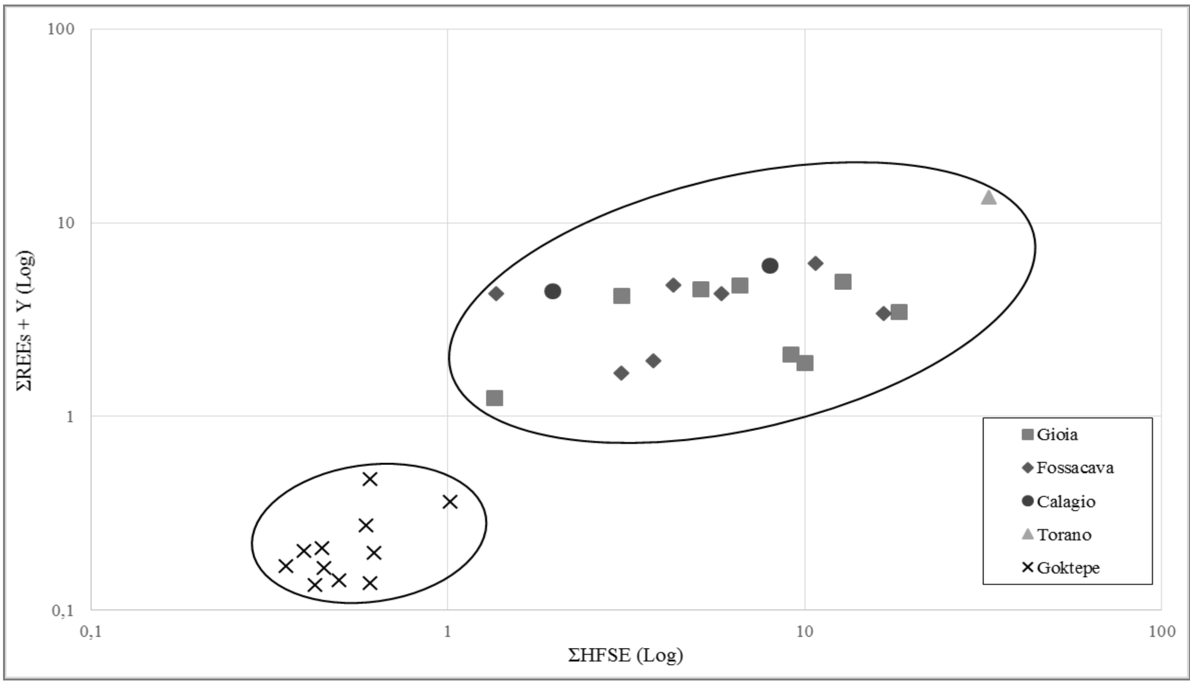

Fig. 4: sum of HFSE (Sc, Th, U, Pb, Zr, Ce, Hf, Ti) *vs* sum of REEs (La, Ce, Nd, Eu, Gd, Dy, Er) +Y content in Carrara and Goktepe samples. Goktepe has the lowest concentrations in HFSE and REEs and the two districts form separate

cluster.

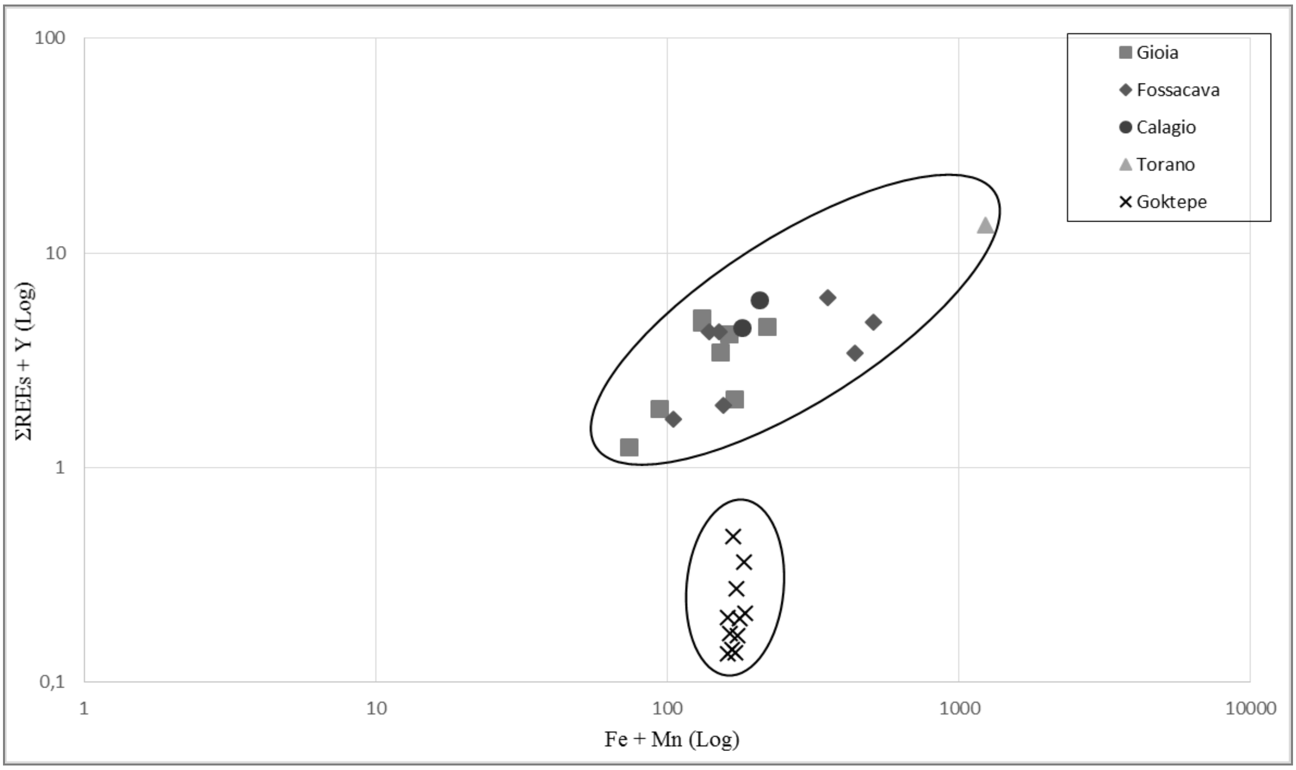

Fig. 5: Fe + Mn *vs* sum of REEs (La, Ce, Nd, Eu, Gd, Dy, Er) +Y content in Carrara and Goktepe samples. Carrara and Goktepe marble fall into separate clusters broadly distinct.

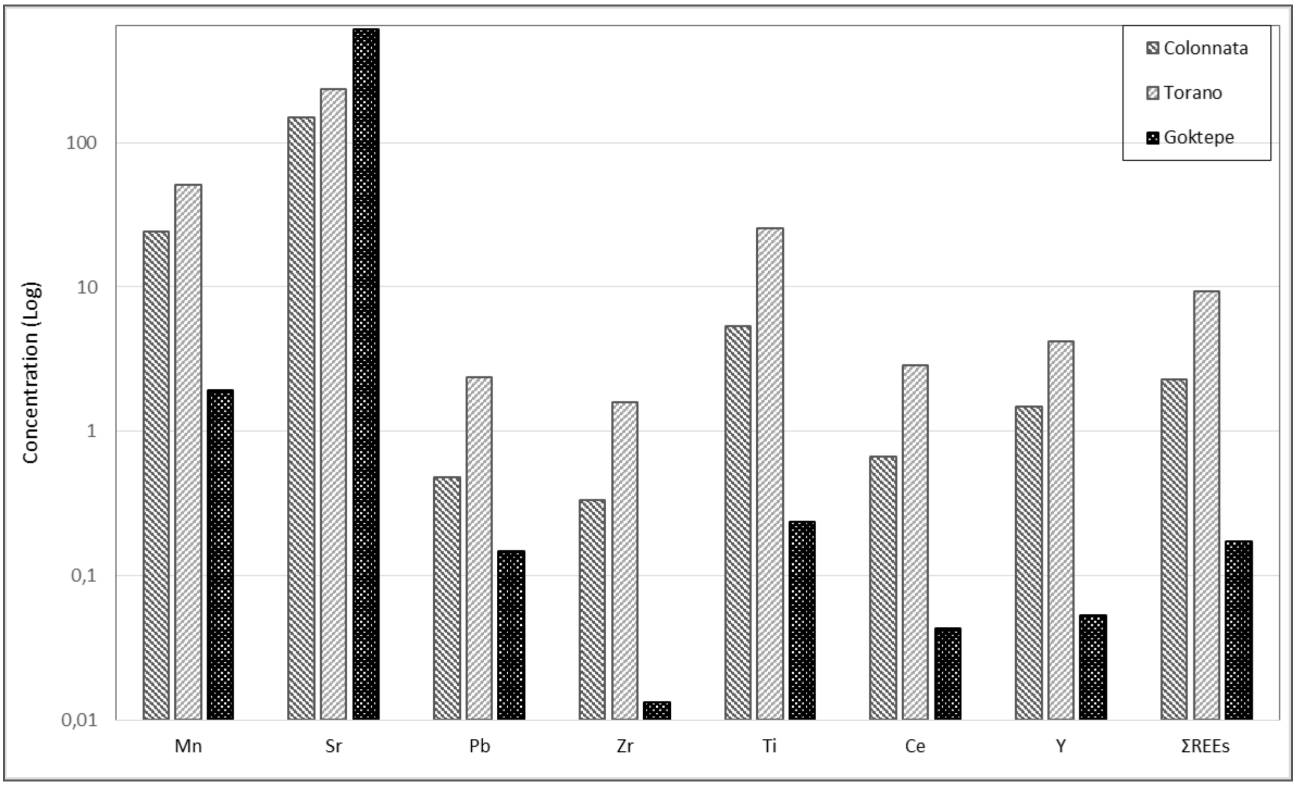

Fig. 6

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