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# UNIVERSITÀ DEGLI STUDI DI TORINO

***This is an author version of the contribution published on:***

*Questa è la versione dell'autore dell'opera:*

*SERRA M., BORGHI A., GALLO L., HOVORIC R., VAGGELLI G. (2010): Petrographic features, genesis and provenance of Pietra Paesina collections of the Regional Museum of Natural Sciences of Turin. Period. Mineral., special issue, 95-111*

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*<http://www.dst.uniroma1.it/riviste/permin/testi/V79.SpecialIssue/2010PM0024.pdf>*

Period. Mineral. (2010), special issue

doi: 10.2451/2010PM0013  
http://go.to/permin

**PERIODICO di MINERALOGIA**  
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*An International Journal of  
MINERALOGY, CRYSTALLOGRAPHY, GEOCHEMISTRY,  
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## Petrographic features, genesis and provenance of Pietra Paesina collections of the Regional Museum of Natural Sciences of Turin.

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*Submitted, - Accepted*

**ABSTRACT** - *Ruin marble* outcropping in central Italy always aroused the contemplative interest of collectors and artists. With his geometrical, vividly edged and irregular colour patterns, this biomicrite, which is worldwide known as *Pietra Paesina*, remind painted landscapes or ruined villages. Even though the first aesthetical descriptions go back to XVII century, it was just in 1970 that Civitelli put a first light on the genesis of the rock, evidencing the non tectonic origin of its structure. Later on, the colour banding was correlated to the so called *Liesegang* phenomenon, with the periodical precipitation of iron oxy-hydroxides following the infiltration of oxidizing ground waters during diagenesis and weathering. This work updates the previous hypotheses and demonstrate the possibility of mapping the concentration of diagnostic elements through different samples from Italian central-northern Apennines (Tuscany, Emilia Romagna, Southern Piedmont) by means of non-invasive techniques. Studying the *Pietra Paesina* ancient stone collections preserved in the Regional Museum of Natural Sciences of Turin, we compared the results of the traditional electron microbeam techniques with those of a bench-top micro-fluorescence instrument. With the limitations linked to the dimensions of the sample chamber, micro-

XRF resulted to be a useful tool for the fully non-destructive analyses, allowing the distinction between different Italian varieties and setting the base for the provenance determination of ancient stone artifacts. Minor and trace elements quantification evidenced Mn, Sr and Ti concentrations as the most discriminatory parameters for provenance identification. Colour changes showed strict correlation to iron content, the percent variations depending on the composition of each sediment. Capillary forces controlling iron precipitation from weathering solutions are strongly influenced by the sedimentary structures, resulting in complex systems of dark bands and modifying the regular periodicity of *Liesegang* patterns.

**RIASSUNTO** - Fin dai primi impieghi documentati in epoca etrusca, la *Pietra Paesina* o *marmo ruiniforme* rappresenta una delle varietà litologiche più rare ed apprezzate dai collezionisti. Petrograficamente si tratta di una biomicrite caratterizzata da un fitto sistema di fratture che delimitano poliedri policromi a ricordare paesaggi turrati o villaggi in rovina. Nonostante le prime descrizioni di questo tipo litologico risalgano al XVII secolo, è stato soltanto all'inizio degli anni '70 che Civitelli ha cercato di far chiarezza in merito alla genesi della roccia, escludendo che il fenomeno della

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cosiddetta *paesinizzazione* dei calcari della Formazione dell'Alberese (Auctt.) possa in qualche modo essere legato ad un processo di fagliamento. Successivamente, attraverso il confronto tra marmi ruinformi di diversa provenienza, si è proposta una correlazione tra la tipica struttura a bande colorate e quello che viene definito fenomeno di Liesegang. Questo lavoro ha avuto l'obiettivo di verificare le precedenti ipotesi su diversi campioni provenienti dall'Appennino settentrionale (Toscana, Emilia Romagna, Piemonte meridionale) ed altresì di valutare la distribuzione spaziale di alcuni elementi particolarmente diagnostici al fine di caratterizzare in maniera univoca diverse varietà italiane. Attraverso l'analisi delle collezioni del Museo Regionale di Scienze Naturali di Torino, si è inoltre rivolta l'attenzione al confronto tra i risultati delle tradizionali tecniche di micro fascio elettronico con quelli ottenibili per mezzo di un sistema di quantificazione non invasivo come la micro fluorescenza a raggio X. Il caratteristico aspetto della *Pietra paesina* è stato correlato in maniera univoca ed in tutti i campioni analizzati alla precipitazione periodica di idrossidi di ferro come conseguenza dell'infiltrazione di fluidi ossidanti durante la diagenesi o più probabilmente per processi di weathering. I sistemi di frattura sin- e post-diagenetici che caratterizzano tutte le varietà oggetto dello studio, sono risultati essere determinanti nel circoscrivere il fronte di avanzamento del fluido all'interno di poliedri definiti dalle pareti di calcite spatica. La mappatura degli elementi maggiori, minori ed in traccia nei diversi sedimenti ha consentito di definire la composizione elementare media delle diverse strutture, identificando nel tenore medio di Sr, Mn e Ti i marker maggiormente discriminanti nello studio archeometrico di provenienza.

KEY WORDS: *Pietra Paesina*, *Micro-XRF*, *Archaeometry*, *Iron oxy-hydroxides*

#### INTRODUCTION

The terms *Pietra Paesina*, *Ruin marble* or *Florence stone*, originally characterizing Tuscan varieties, are now commonly used to define marly limestones and limestones whose intense fracturing define vividly coloured patterns reminding landscapes, abstract paintings or

ruined villages. The macroscopic aspect is due to the rhythmical precipitation and consequent enrichment in iron and manganese oxy-hydroxides.

Though the use of *ruin marbles* is documented at least since Late Helladic in Mycenaean Greece (i.e. Mycenae, on the northwest fortification walls, 13th century B.C.) and Etruscan civilization (Grubessi, 2010), the first description of this precious and rare figure stone was made in the half of XVII century in Kircher's "Mundus subterraneus" (1664). Since that moment, the interest on this figure stone spread in France, Germany and England but it was just in the beginning of XIX century that *ruin marbles* began to be used for the production of veritable natural figurative paintings (Gallo, 1995). As the collectible interest in the stone arose, different varieties have been identified in Central-Northern Apennines, allowing the definition of different commercial names linked to the main chromatic features, such as *Verde d'Arno*, *Lineato d'Arno*, *Tigrato d'Arno* and *Terra Bruciata di Rimaggio*.

Despite collectible interest and artistic description, the rock has been poorly studied from a scientific point of view. The same origin of the stone is still debated. For a hundred year, in fact, the phenomenon of the coloured bands formation was connected to a process of faulting in weathered limestones. It was just in the beginning of '70 that Civitelli et al., studying Paleocene samples from Central Italy (Monti Lepini and Monti della Tolfa), put a first light on the genesis of *Pietra Paesina*. On the base of structural observations, they excluded the possibility of a tectonic origin of the coloured patterns (Civitelli et al., 1970). Despite, they suggested the offset of the bands to be just apparent, noticing the absence of offset in the rock layering. A further work confirmed these results on samples collected in Tuscan-Emilian Apennines (Daniele et al., 2006).

The purpose of this paper is to proof the

previous hypotheses about the genesis of *ruin marbles* and to extend the scientific study of Italian varieties through the analysis of some of the most representative samples of the Regional Museum of Natural Sciences of Turin (Mineralogy, Petrography and Geology section). The still growing collections preserved in Turin (Gallo, 1992, 1995 and 1996, Gallo and Fiora, 1998) cover a period from eighteenth century and comprehend over 150 samples from different Italian regions with a widespread variability of aesthetical and geochemical features. Accordingly to conservative requirements, we have limited the sampling to the materials which displayed key features to understand the genesis of the rock. The analysis of these samples provided useful information to test the potential of a non-invasive approach for the geochemical characterization of the collections preserved in the museum. Therefore, the investigation on *ruin marbles* supplied a

chance to improve and develop micro-XRF application to valuable cultural heritage.

This work represents a preliminary step of a wider research that will deepen into the mineralogical investigation on colour variability of iron precipitates with the final goal to provide and exhaustive characterization of Italian *ruin marbles*.

#### GEOLOGICAL SETTING

Even though *ruin marbles* were identified in Monti Lessini (Fabbian, 2006), Elba island (ibid.), Western Liguria (samples in the Regional Museum of Natural Science, Torino) and Bergamo (Paganoni e Camerlenghi, 1987), most of the best known Italian varieties come from Northern Central Apennine, with particular reference to Emilia, Tuscany and Lazio regions (Fig. 1). They are varieties of fine-grained limestones with a close spaced system of healed

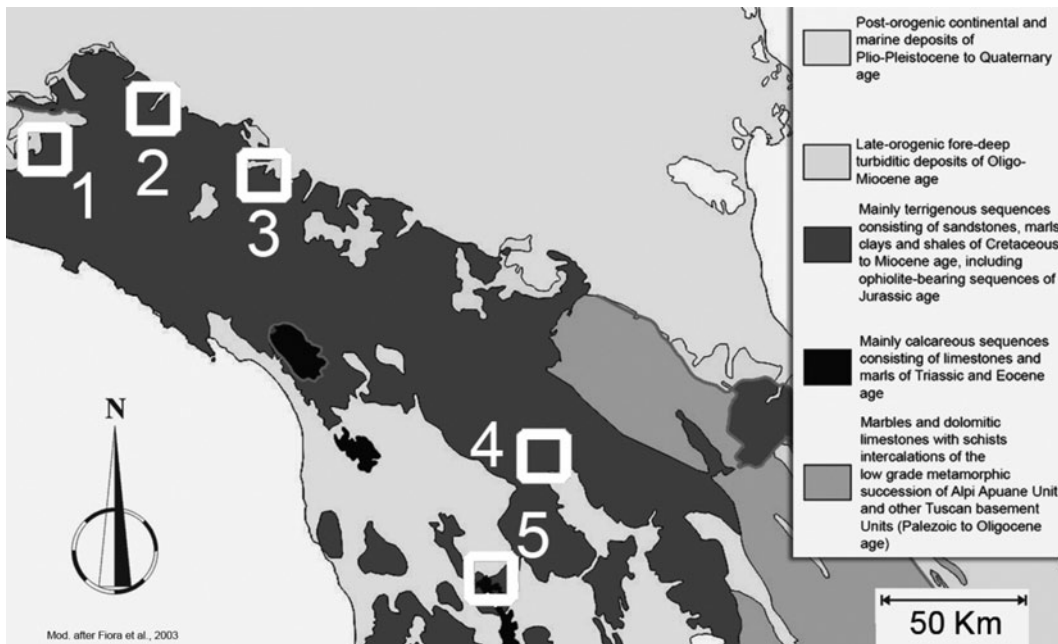


Fig. 1 - Provenance of the investigated *ruin marbles* in the Italian North-Central Apennines: Val Curone (1), Val Trebbia (2), Val di Taro (3), Valdarno (4) and Val d'Arbia (5). Modified after Fiora *et al.* (2003).

joints, which define independent polyhedra marked by characteristic brownish colour bands. The typical aspect of rocks is generally highlighted and enhanced for artistic purposes by cutting and polishing weathered blocks or boulders.

Considering their historic importance, our attention has been focused primarily on the

different Tuscan varieties, coming the south-east of Florence (Fig. 1 and 2a). They belong to the Monte Morello Formation, which consists of marly limestones, calcarenites and clays alternation (Merla *et al.*, 1967).

Similar macroscopic features characterize the marly limestones of the Bettola Flysch (cfr. Monte Caio Flysch, Boni *et al.*, 1971). They

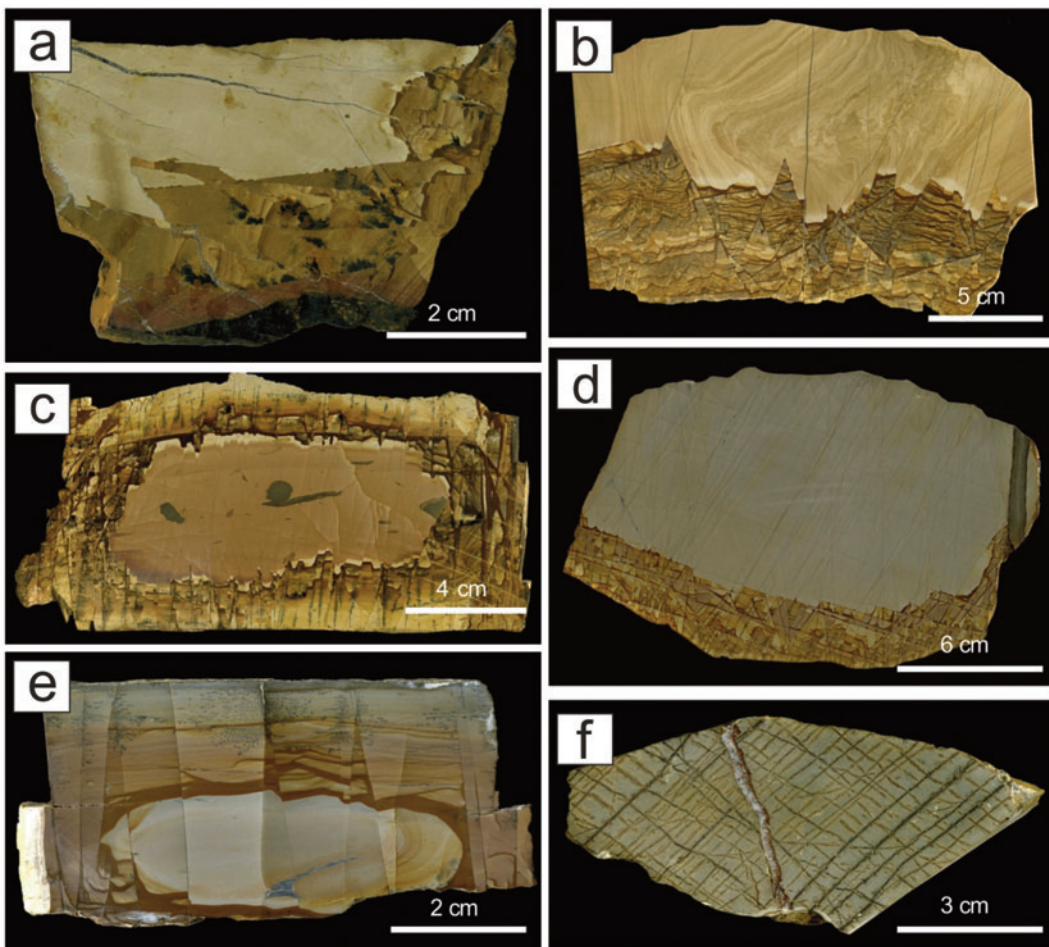


Fig. 2 - Representative polished sections of the different varieties. Valdarno (A) Val Trebbia (B) and Val di Taro samples (C) display brownish tints, the last ones being characterized by closely spaced systems of joints and evident manganese dendrites. Piedmont ruin marbles (D, E) show darker colours with a close system of bands varying from brown to dark violet. Val d'Arbia samples (F) can be clearly distinguished by their greyish tints, the absence of colour banding and the closer millimetre scale system of orthogonal bands.

belong to a carbonate-marly turbiditic sequence of Upper Cretaceous - Eocene age outcropping in Northern Apennines (Di Dio et al., 2005). Samples preserved in the Museum were collected few kilometers south-east of Piacenza, at Rezzanello, in Trebbia Valley (Fig. 1 and 2b). Emilia-Romagna region is represented also by samples coming from central Taro valley (Fig. 1 and 2c), south of Parma, in an area comprehended between Fornovo and Baldo.

In order to test the genetic hypotheses and to complete the selection of the most representative stones of the collections, rare Piedmont *ruin marbles* (Val Curone) were included in the studied varieties. They were identified in Caio limestones (Bellinzona *et al.*, 1971) and collected in the south-east of Alessandria (Fabbian, 2006, Fig. 1, 2d and 2e). Piedmont varieties can be distinguished by the different colour of the not-altered sediment corresponding to a different clay-carbonate ratio.

The varieties coming from Murlo Formation (Signorini, 1967), south east of Siena (Fig. 1), display different macroscopic features, being characterized by a closer spacing of the double system of joints and the absence of a clear colour banding (Fig. 2f).

#### MATERIALS AND METHODS

The collections preserved in the Museum provide the possibility to take advantage of a widespread sampling of the different Italian *ruin marbles*. The first step of the research was therefore the selection of samples which could best display the genesis of the stone with all his declinations in shape and colour. Eight samples were chosen for the non-invasive analytical work, keeping into account the polishing and the characteristics of the surface. Structural observations were based on macroscopic study under a binocular microscope. The morphological and geochemical features of the hand specimens were studied through a scanning electron

microscope (SEM; Cambridge Stereoscan S360), equipped with an energy-dispersive spectrometer (EDS; Oxford Instruments). An accelerating voltage of 15 kV and a livetime of 60 sec were used. The evaluation of iron and oxygen variations through the samples was made setting the analytical condition to 8kv with SPI53 mineral phase standards (calcite, dolomite, diopside, quartz, goethite and hematite) for quantitative mapping.

Major elements EDS quantification was used as a matrix correction for micro X-ray fluorescence analysis (micro-XRF Eagle III-XPL, Röntgenanalytik Messtechnik GmbH, Germany). For the specific purposes of our research, XRF spectra were acquired using primary beam filters in order to minimize diffraction peak artifacts and to optimize peak to background ratio. The choice of specific filters was made to enhance particular regions of the spectra according to the expected trace elements in the matrices. Poly-capillary lens (30  $\mu\text{m}$ ) was used to collimate the microbeam at the sample surface.  $\mu\text{-XRF}$  data on major and trace elements were acquired for 1000 s, with a titanium 25  $\mu\text{m}$  thick primary filter, a probe current of 40 kv and an accelerating voltage of 1mA. Fundamental parameter quantification method was integrated with ALV981 (Fine and Stolper, 1986, Metrich and Clocchiatti, 1989) and NIST SRM 610 and 612 (Pearce *et al.*, 1997) standards for the quantification of major and trace elements.

Finally, in order to test the genetic hypotheses and to deepen into the petrographic study, the most representative sample from Tuscan-Emilian Apennine (TE1A) was chosen for a mineralogical and paleontological investigation. The sample was prepared as polished thin section for polarizing microscope and SEM observations. Photomicrographs were taken using a CCD camera.

Diffraction patterns were acquired by a Bruker AXS D8 Advance diffractometer equipped with a Cu  $K\alpha$  radiation source and diffracted beam

graphite monochromator with a  $0.1^\circ$  step. Iron oxy-hydroxides were identified after dissolution of the carbonate fraction by means of HCl aqueous solution (5%).

On a first approximation, iron content in EDS and XRF elemental profiles was recalculated as  $\text{Fe}_2\text{O}_3$  according to diffractometric results.

#### LITHOLOGY

All the studied rocks are chiefly composed of micritic calcite, remnant of planktonic foraminifera and variable amount of clay minerals and silt-size quartz.

In agreement with previous observations on Alberese limestones (Civitelli *et al.*, 1970), microfossil records are mainly represented by planktonic foraminifera and fragments of gastropoda. Dinocysts have also been identified.

Even though joint morphology and distribution, shape and chromatic features show a widespread variation making a unique piece of every figure stone of the collection, it is possible to distinguish samples of different provenances according to major and trace elements composition of the un-weathered core, which, in most cases, resulted representative of the original sediments.

In fact, despite the local varieties classified with different commercial names, geochemical data, acquired by a non-invasive procedure, showed a relative uniformity in the different source areas, allowing a subdivision of the samples according to their provenance.

All samples coming from Tuscan - Emilian Apennine (Val Trebbia, Fig. 2b and Val di Taro, Fig. 2c) are characterized by an higher carbonate concentration, resulting in an average calcium oxide content on the whole rock of 87 wt.% (TABLE 1, Fig. 3a). Silicate minerals are limited to rounded quartz grains, 10 and 60  $\mu\text{m}$  in size. These features result in macroscopically lighter colour and a beige-yellowish tint of the un-weathered sediment. Trace elements

investigation showed a relatively constant Sr content, with an average concentration of 230 ppm (TABLE 1, Fig. 3b). As compared to Val Trebbia samples, Val di Taro *ruin marbles* are characterized by a higher Ti (>1000 ppm) and a lower Cr content (<60 ppm) (TABLE 1).

Valdarno samples, coming from the southern surroundings of Florence (Fig. 1, 2a), can be distinguished for higher clay minerals content, with a rather stable  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  concentration, respectively varying from 28.3 to 32.1 wt. % and from 2.6 to 2.8 wt. % (TABLE 1, Fig. 3a). These samples provide the opportunity to test the effectiveness of the provenance characterization method, as the elemental composition displays slight changes despite highly variable morphology and colour.

Similar features characterize south Piedmont fine-grained clayey limestones (Fig. 2d and 2e), which are marked by a lower manganese concentration, resulting in an average MnO content of about 0.1 wt. % (TABLE 1). The distribution of micrite vs. clay fraction can be argued from fig. 4, where  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  content in Val Curone limestones (Fig. 4a) is compared to that of Val Trebbia samples (Fig. 4b). The images give an idea of the distribution of the silicate fraction in the sediment, which consists of individual grains both of rounded shape quartz and elongated feldspars (mainly pure albite). The geochemical features result in a macroscopically light gray colour of the sediment, which is characteristic of all Val Curone *ruin marbles*.

The macroscopic differences of Val d'Arbia samples find a clear correspondence in geochemical features. The rock is marked by two orthogonal systems of joints and by the absence of a distinctive colour banding (Fig. 2e). The sediment is composed by a higher clay fraction, which results in a different  $\text{Al}_2\text{O}_3$  concentration, ranging from 16.1 wt.% to 17.8 wt.%. Accordingly, trace elements are significantly different from all the other samples, being characterized by a higher Ti content (average 0.3

TABLE I  
 $\mu$ -XRF representative analyses of some of the studied samples. C = light colour central part; LB = light colour interspaces between the dark bands DB = dark bands.

Samples	MgO [wt. %]	Al <sub>2</sub> O <sub>3</sub> [wt. %]	SiO <sub>2</sub> [wt. %]	P <sub>2</sub> O <sub>5</sub> [wt. %]	CaCO <sub>3</sub> [wt. %]	K <sub>2</sub> O [wt. %]	MnO [wt. %]	Fe <sub>2</sub> O <sub>3</sub> [wt. %]	Tot	Ti [ppm]	Sr [ppm]	Cr [ppm]	Zn [ppm]
TE2C/C	1.27	0.99	1.12	0.17	95.38	0.08	0.25	0.53	99.79	386	192	26	28
TE2C/LB	1.13	1.15	1.21	0.19	88.91	0.08	0.37	6.02	99.07	630	228	48	30
TE2C/DB	1.64	1.18	2.40	0.18	79.80	0.11	0.35	13.40	99.05	669	203	53	36
TE1A/C	0.79	2.00	4.72	0.18	90.59	0.18	0.22	1.04	99.72	1031	258	46	25
TE1A/LB	0.68	1.93	4.29	0.19	84.37	0.18	0.55	6.87	99.05	1196	246	54	25
TE1A/DB	2.03	1.71	2.73	0.17	78.05	0.15	1.09	13.09	99.02	1349	217	98	bdl
P2A/C	1.32	5.01	36.05	0.10	52.70	0.45	0.19	3.86	99.67	1169	263	47	bdl
P2A/LB	0.97	3.72	36.91	0.11	50.72	0.46	0.17	5.42	98.47	1277	260	59	bdl
P2A/DB	0.77	4.00	35.10	0.10	49.39	0.44	0.14	8.50	98.45	1392	261	81	bdl
P2B/C	1.33	4.01	41.45	0.10	47.98	0.51	0.13	2.96	98.49	1200	232	42	bdl
P2B/LB	1.13	3.61	40.06	0.10	47.08	0.45	0.13	5.94	98.49	1192	240	60	bdl
P2B/DB	1.10	3.20	37.01	0.10	47.25	0.38	0.14	9.29	98.47	1306	246	89	bdl
F11A/C	1.03	2.64	28.81	0.14	63.27	0.08	0.19	3.39	99.56	1880	208	41	28
F11A/LB	0.99	2.66	29.72	0.14	61.11	0.08	0.27	4.71	99.67	1170	206	48	31
F11A/DB	0.96	2.76	28.22	0.13	57.33	0.10	0.21	8.76	98.48	1283	201	77	36
S11A/C	2.10	15.27	37.50	0.06	36.69	1.17	0.16	5.31	98.27	2622	67	60	35
S11A/LB	2.13	16.45	35.00	0.07	37.48	1.22	0.15	5.77	98.26	2628	79	65	31
S11A/DB	2.82	16.49	33.17	0.06	36.91	1.25	0.20	7.32	98.23	2812	85	79	32

bdl = below detection limit

wt.%, TABLE 1, Fig. 3b) and significant reduction of Sr, which never exceed 90 ppm. The average concentration of MnO (0.2 wt.%) is strongly influenced by the distribution of iron precipitates, which are widespread in the sediment without any preferred periodical system. In this specific case, the pervasive alteration, linked to the close system of joints, exclude the possibility to characterize the unweathered sediment.

#### STRUCTURAL OBSERVATIONS

All the samples were investigated from a structural point of view on a macro- and mesoscopic scale. Tuscan-Emilian samples underwent a deeper investigation through thin section polarizing microscopy.

*Pietra Paesina* can be generally classified as a bioclastic wackestone/mudstone (Dunham, 1962) with variable amount of clay minerals, which influence the chromatic features of the unweathered sediment. Most of the analyzed hand specimens show an external part interested by a pervasive alteration and a central part, with variable wide and shape, which is not macroscopically modified by weathering processes. This evidence is confirmed by field observations on the original sediments.

With the exception of the dense and regular network of joints in Val d'Arbia samples, all investigated *ruin marbles* are marked by different generations of joints and micro-veins. Joints are organized at least in two systems filled by blocky calcite. The thickness varies from 100

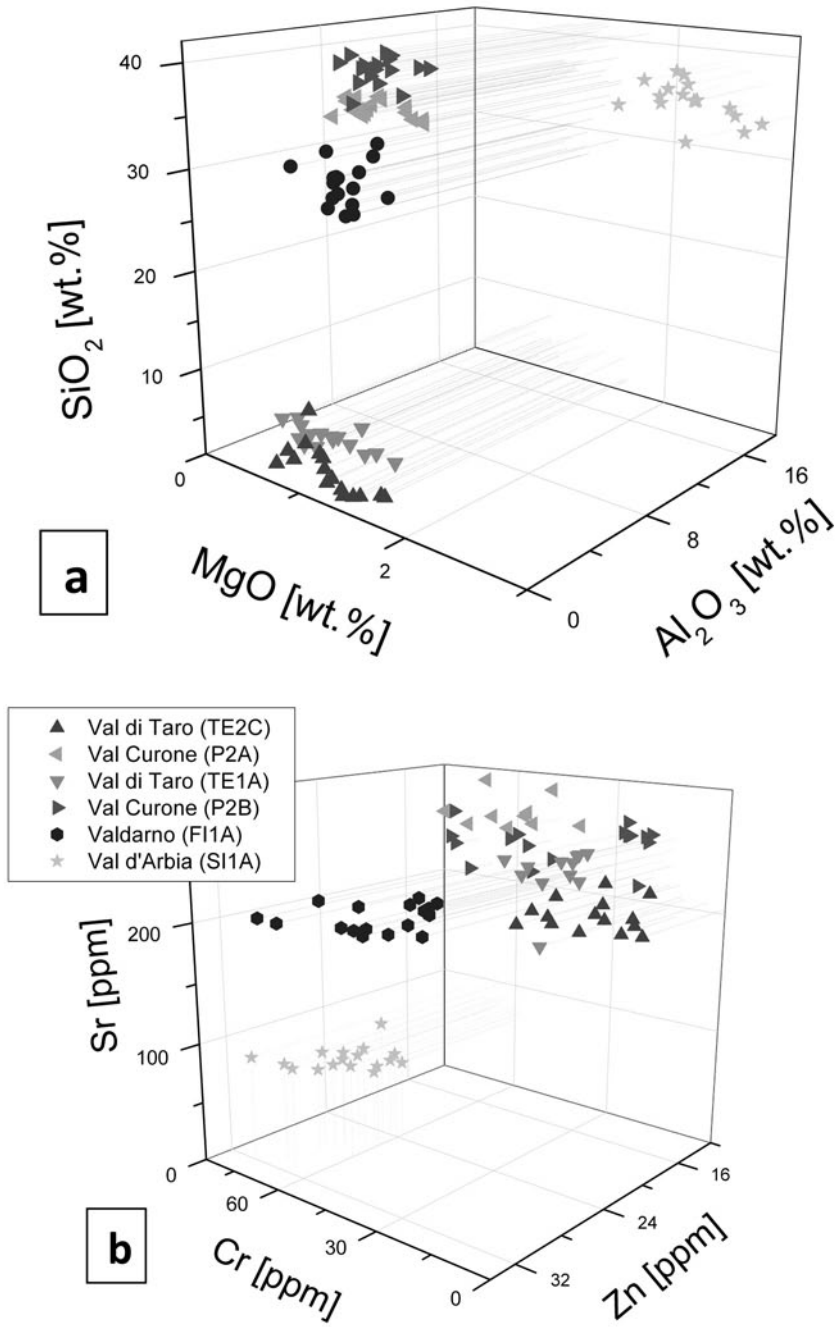


Fig. 3 - Major (A) and trace (B) element average composition ( $\mu$ -XRF) of the different varieties of *Pietra Paesina*.

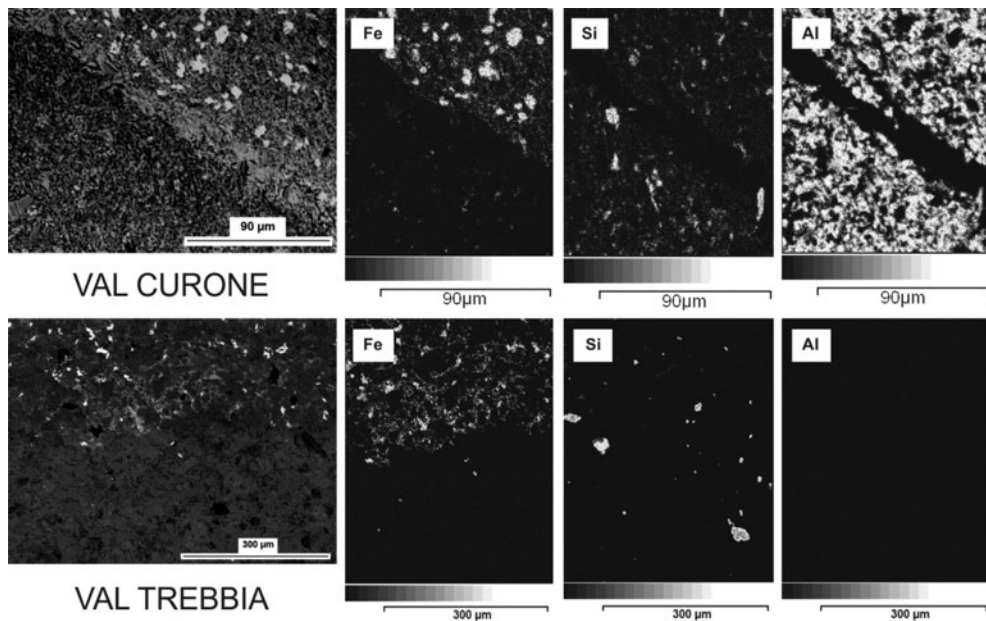


Fig. 4 - BSE images of Val Curone (A) and Val di Taro (B) polished sections. The selected area crosscut healed joints separating macroscopically light and dark zones. Si, Al and Fe EDS mapping underline the differences in sediment composition together with the variations in iron relative amount through the samples.

to 300 µm. Microscopic scale observations allowed the clear distinction between the different systems. An earlier generation of stilolitic joints (Fig. 5, J1) show extremely variable thickness (up to 300 µm), the diameter of calcite crystals being strictly correlated with the width of the joints. Stilolites crosscut the sediment without causing breaking of the grains (Fig. 5a and 5b) and are parallel or subparallel to sediment lamination.

Later conjugate system of joints (Fig. 5, J2) tends to develop with a high angle to rock bedding (Fig. 5c), being nearly straight and cutting the earlier leptoclases (Fig. 5a, 5b and 5d). Healed joints diameter is in general comprehended between 100 and 500 µm. Even though on a macroscopic scale these fractures could be interpreted as a system of faults, all examined samples clearly show the absence of offset of rock bedding at the joints and between

intersecting joints. Moreover, as already underlined by Marko *et al.* (2003), joints often show a non-penetrative character (Fig. 5d), being organized in independent overstepping segments (Fig. 5e).

Younger healed joints develop from the border to the core of the boulders, showing variable width and radial spreading. These last seem to have developed in a late stage, generally postdating colour banding (Fig. 5, J3).

#### COLOUR BANDING

One of the most characteristic features of *Pietra Paesina* is the presence of a distinctive colour banding resulting in alternating patterns varying from the most common dark brown, to less frequent dark red, green and violet tints. The bands are parallel or sub-parallel to the surface of the rock boulders and generally follow the

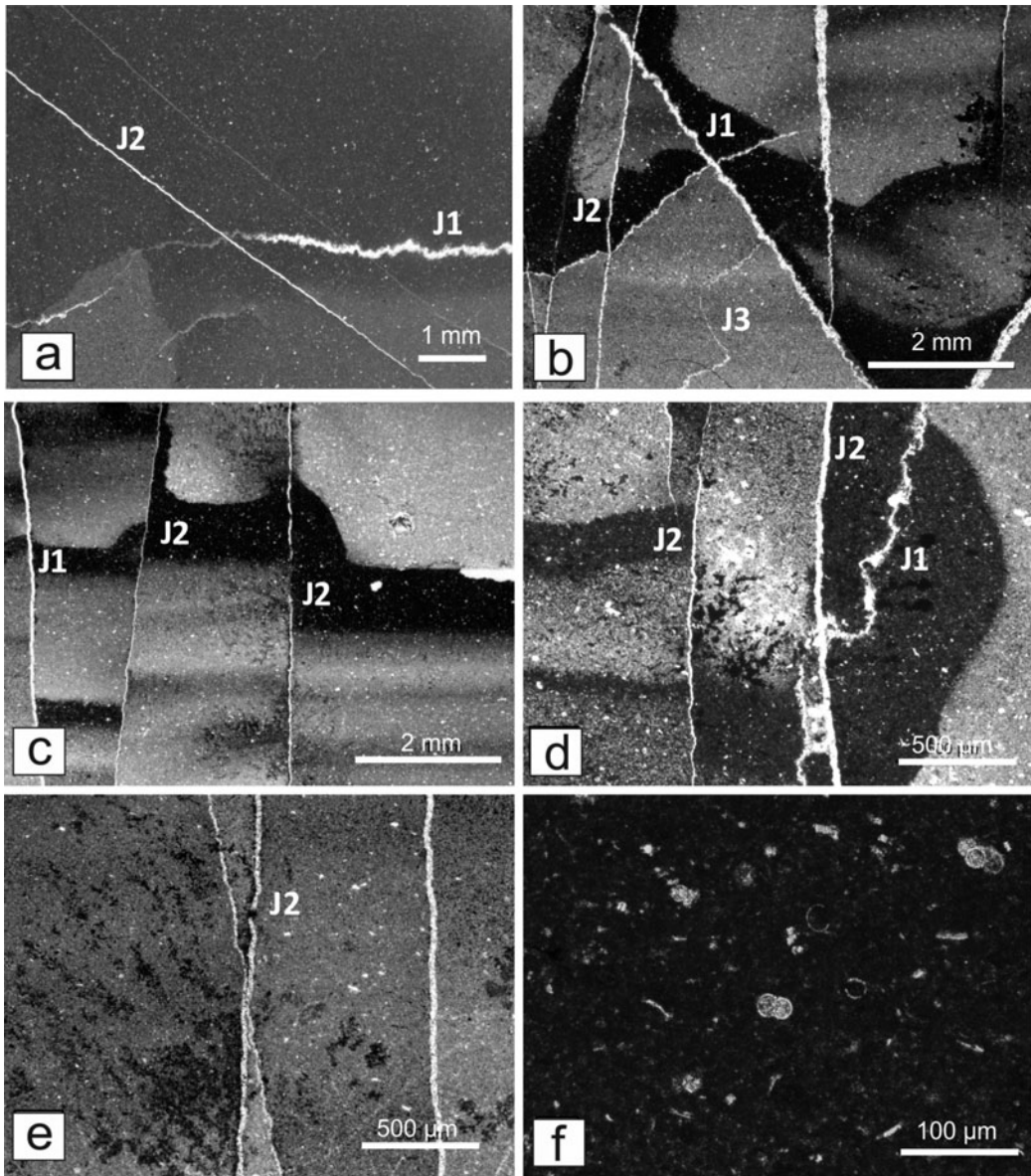


Fig. 5 - Thin section polarizing microscope images display some structural features of representative Tuscan Emilian Apennine samples. A, B, E) Stilolites (J1) crosscut by younger joints (J2). Plane polarized light. B) Spatial relations between the different generations of joints (J1, J2 and J3), showing the absence of offset at the intersection of coeval pairs. Plane polarized light. C) Detail of colour banding with apparent offset of the bands and typical single or double concave shape of the external surface in contact with the joints. Crossed polarized light. D) Apparently conjugate healed joints and distribution of Mn-dendrites. Plane polarized light. E) Sub-parallel healed joints (J2) crosscut earlier stilolite-like leptocones (J1). Plane polarized light. F) Micropaleontological record represented by planctonic foraminifera, dinocysts and fractures of closely unspecified exoskeletons of gasteropoda. Crossed polarized light.

discontinuities determined by rock bedding and lamination. Most frequently the bands display independent patterns in the polyhedra defined by healed joints, giving the impression of being offset by a strike-slip system of faults (Fig. 2). No offset of the lamination accompanied offset of the colour patterns. Moreover, some of the studied samples do not show offset of the bands along the joints. The thickness of the bands in the examined samples varies from few micrometers up to 5 mm and tends to increase moving from the border towards the centre, generally reaching a maximum corresponding to the ellipse defined by the pale tint central part of the boulders.

Single or double concave shapes have often been observed on the external border of the bands in contact with the joints (Fig. 5c).

In order to better understand the processes leading to the creation of colour banding, to

proof elemental analysis results and to identify iron oxy- hydroxide precipitates, one of the most representative ruin marbles (Fig. 2b) underwent a mineralogical investigation. Tuscan-Emilian samples were selected for powder diffraction analyses as they display simpler carbonate matrices with lower amount of silicate mineral phases which could infer the interpretation of diffraction patterns. According to the EDS and  $\mu$ -XRF elemental data deductions, powdered dark bands resulted to be composed of calcite, quartz and goethite.

Selective dissolution of the carbonate fraction improved the lower intensity XRD peaks visibility allowing the identification of illite and akaganeite together with already observed quartz and goethite (Fig. 6). Due to the chosen analytical procedures, the identification of low intensity illite diffraction peaks cannot be considered as representative of clay mineral

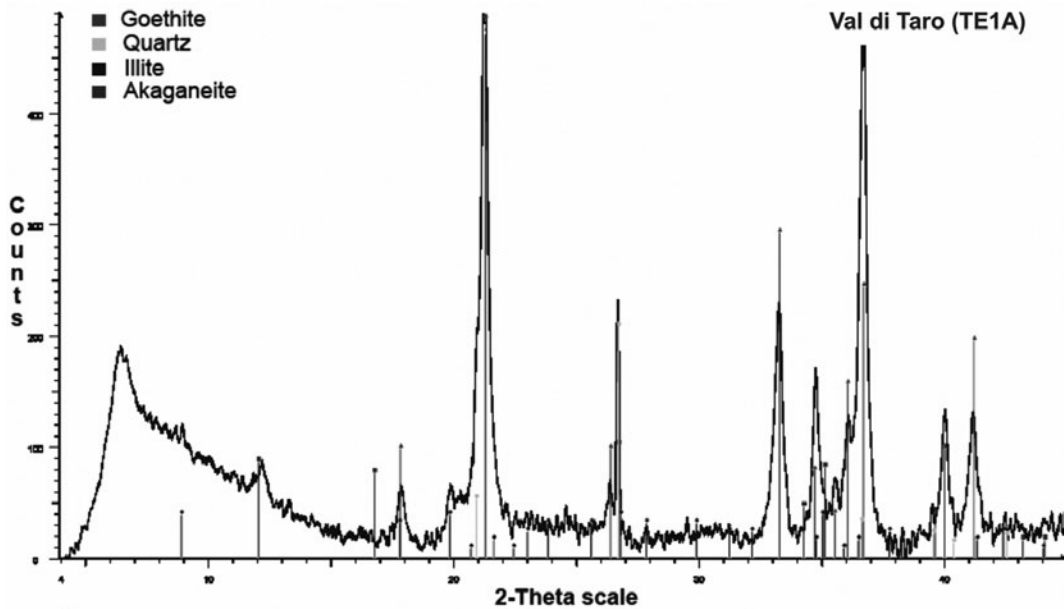


Fig. 6 - X-ray diffraction pattern of Val di Taro (TE1A) sediment after selective dissolution of the carbonatic fraction.

phases characterizing the sediment. The presence of akaganeite, never evidenced before in *ruin marbles*, can be caused by recrystallization of goethite with increase of acidity during selective dissolution of calcite.

Not evidencing any iron gradient between light core and dark brown bands, previous works (Civitelli et al., 1970, Daniele et al., 2006) suggested goethite to be the product of iron oxidation due to meteoric waters circulating at the surface, without any external source.

XRF linescans performed along the core through the dark coloured bands allowed quantitative mapping of the elemental variations towards the samples (Fig. 7a). Banding resulted to be strictly linked to iron concentration (Fig.

7b), notwithstanding colour changes (from dark brown to dark red and greenish brown) through each sample and between different samples. This consideration suggests the chromatic variations of the dark bands to be linked to changes in crystalline structure of precipitates and possibly iron oxidation state.

Val di Taro samples are characterized by the most significant gradient, passing from average 0.5 wt. % of the light core to 13.4 wt.% of the darkest bands (TABLE 1, Fig. 7b).

According to previous observations, Val Curone and Valdarno samples result richer in clay fraction and with higher average iron content. The variation is therefore less evident, the darker part being 2 to 3.5 times richer in Fe.

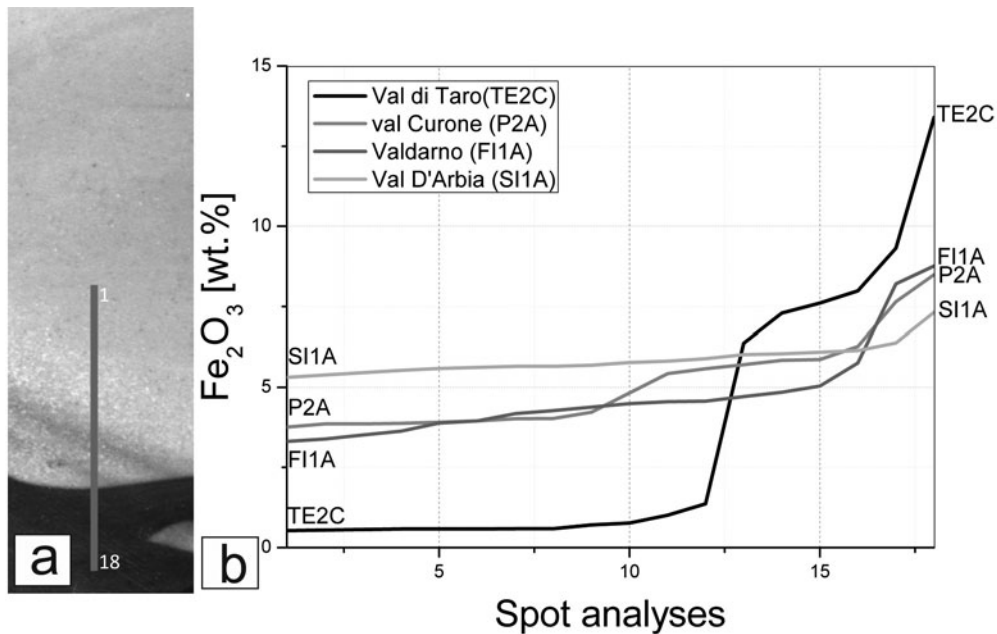


Fig. 7 -  $\mu$ -XRF linescan profiles (18 spot analyses on 2 mm lines), showing the iron variations (A) from the light core to the inner dark band. Iron content has been recalculated as  $\text{Fe}_2\text{O}_3$  wt.%. Val di Taro samples display the highest gradient, passing from mean 0.5 wt. % of the core to 13 wt. % of the brown band. On the contrary, Piedmont and Valdarno biomicrites result to be averagely richer in iron, showing smaller variations, from 3.3 wt.% to 8.5 wt.%. Siena varieties (Val d'Arbia) are characterized by a medium concentration ranging from 5.5 wt.% to 6.6 wt.%, with a slight increase of iron content in close proximity to the joints.

Maximum iron concentration, recalculated as  $\text{Fe}_2\text{O}_3$ , never exceed 9.5 wt.% (TABLE 1, Fig. 7b).

An exception is represented by Val d'Arbia samples. In this case, the absence of a clear banding results in a averagely higher iron content, which is comprehended between 5.4 and 7.3 wt. % (TABLE 1, Fig. 7b). The highest values were observed in correspondence or in close proximity to the joints.

Moving from the light core to the dark bands, iron increase is accompanied by contextual manganese (MnO wt.%) increase. MnO concentration varies from 0.2 to 1.1 wt.% in Emilia sample, from 0.1 to 0.3 wt% in Piedmont and northern Tuscany samples. Val d'Arbia samples show an average MnO content of about 0.2 wt.% (TABLE 1).

Linescan profiles across the weathered external part of the boulders and though the inner light core were compared in order to understand the mobility and the source of the elements responsible for colour banding. Fig. 8a displays a representative profile on Val Curone sample. According to the elemental average composition, the outer zone results to be richer in Si and Mn (Fig. 8c), while iron content is averagely lower (Fig. 8b). In the weathered surface, iron results to be concentrated in isolated grains, which were identified by EDS investigations as pyrite and siderite.

#### DISCUSSION

For more than a hundred years, the typical aspect of this rare figure stone has been explained as the result of a process of strike-slip faulting which offset preexisting colour bands. Even though macroscopic observations seemed to support this hypothesis, micro-structural and geochemical results on the studied samples do not fit this model, supporting, on a wider scale, the conclusions achieved by Civitelli *et al.* (1970).

McBride (2003) updated the previous hypotheses, describing the rhythmicity of the

bands as a manifestation of "Liesegang phenomenon" (Liesegang, 1913), with the periodical precipitation of iron hydroxides though diffusion processes in porous media (Henisch, 1988). Accordingly to prior results, Marko *et al.* (2003) described the process on Western Carpathians *ruin marbles*, experimentally proving the feasibility of Liesegang model.

Notwithstanding local differences in the maturity and composition of each sediment, all the samples show common features supporting a unique interpretation for the genesis of ruin marbles.

Structural observations on the hand specimens allowed to distinguish at least three different generations of joints, the first one (Fig. 5, stilolites J1) having formed in an early stage of burial diagenesis.

According to previous conclusions (Marko *et al.*, 2003), later joints (Fig. 5, J2) formed on the already lithified sediment due to increasing fluid pressure developing in one or two conjugate systems, soon filled with sparry calcite.

Fracturing of the rocks and consequent formation of variable sized boulders is responsible for the formation of a third system of joints, whose radial orientation seems to be connected to weathering processes (Fig. 5, J3).

Both meso- and microscopic observations on all the available hand specimens agree with the hypothesis of a non-tectonic origin of the joints, which seem to be most likely linked to syn-sedimentary and exogenic processes.

Diffusion of high fugacity fluids can satisfactory explain, from a geochemical point of view, the periodic and rhythmic precipitation of ferric oxy-hydroxides (Fig. 9).

The fluid front propagation develops according to the independent volumes defined by sparry calcite.

Capillary forces controlling the process change according to the sediment discontinuities, leading to the irregular width of the bands. Thicker bands are generally connected to

variations in grain size and organic fraction concentration (Fig. 5f). As a result, Liesegang banding is strongly influenced by sediment discontinuities, which act as preferred sites for the precipitation of iron oxidic phases.

The dominance of capillary forces is demonstrated also by the concave shape of the bands in contact with the external walls of the joints. Even though a clear gradient in iron concentration accompanies colour banding, a

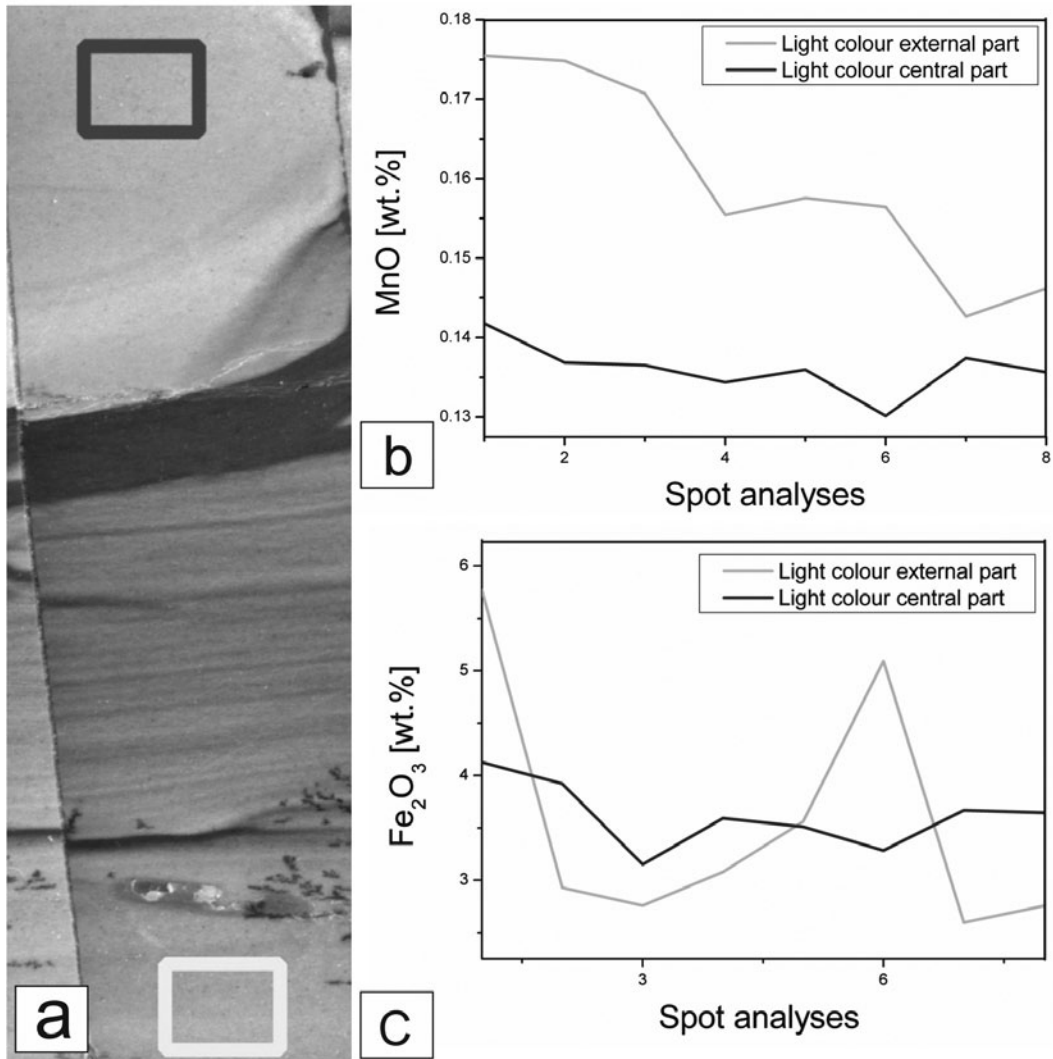


Fig. 8 -  $\mu$ -XRF profiles (A) of the outer border and the inner light core of a *ruin marble* boulder (Valdarno). 8 spot analyses along the 1.7 mm diagonal of the rectangles. A distinctive gradient in MnO concentration (B) suggests the external infiltration of manganese-rich solution. On the other side, iron content (recalculated as Fe<sub>2</sub>O<sub>3</sub> wt. %) (C) is averagely lower in the rim and concentrated in single pyrite and siderite grains, supporting the hypothesis of the absence of an external source of this element in solution.

deeper comparison between the weathered border of the boulders and the inner central part seems to exclude an external source of this element.

On the contrary, manganese linescans suggests the hypothesis of a late stage of circulation of Mn-rich fluids, which is confirmed also by the precipitation of manganese dendrites characterizing most of the studied samples.

#### CONCLUSIONS

The chemical investigation, together with structural and mineralogical considerations, helped proving the previous works about the genesis of *ruin marbles*.

The availability of the collections preserved in the Regional Museum of Natural Sciences allowed to take advantage of a significant

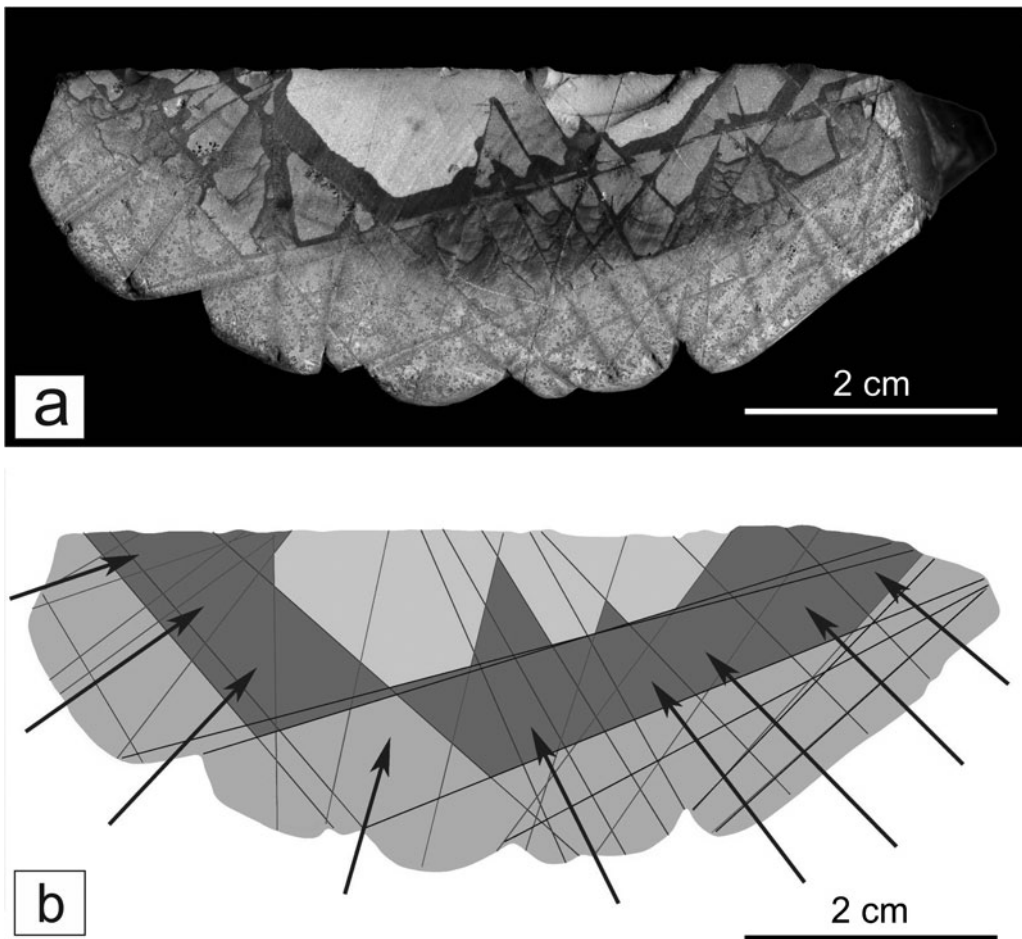


Fig. 9 - Sample F11A (A), coming from south-west of Florence, clearly enlightens the genesis of the rock. The scheme (B) evidences the systems of joints and the direction of high fugacity solution infiltration. Fluid front propagates according to the polyhedra defined by the joints, with preferred directions through the narrow fissures defined by the newly formed calcite (Marko *et al.*, 2003).

sampling of the main Italian varieties and gave the possibility to provide new scientific data about precious stones whose description was limited to collectors' interest and aesthetical appreciation.

*Pietra paesina* definition refers to weathered blocks of fine-grained limestone composed of variable amount of clay minerals and remnants of calcareous organisms (mainly planktonic foraminifera).

Structural and geochemical evidences suggest the origin of all the investigated Italian varieties to be linked to iron and manganese periodical precipitation in the independent polyhedra defined by different generations of healed joints. The phenomenon can be explained by weathering processes with the diffusion of meteoric waters from the exposed surface of already formed rock boulders.

A final consideration deals with the methodological approach. The results of the research suggest the possibility to characterize, according to chemical markers, macroscopically similar stones coming from different geological units or from different areas of the same unit.

The non-invasive character of  $\mu$ -XRF elemental investigation seems to open interesting possibilities when the archeometric goal is to define the provenance or possibly to authenticate high value stone artifacts.

#### ACKNOWLEDGEMENTS

We are grateful to anonymous referees for their helpful comments which have improved this contribution.

Giancarlo Fabbian (Ivrea) and Lorenzo Gallerini (Firenze) provided fundamental information about the provenance of the studied samples.

X-ray fluorescence measures have been obtained with the equipment acquired by the Interdepartmental Center "G. Scansetti" for Studies on Asbestos and Other Toxic Particulates with a grant from Compagnia di San Paolo, Torino, Italy.

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