

## Provenance of materials employed in the construction of Orvieto Cathedral (Umbria, Italy)

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Submitted, January 2000 - Accepted, April 2000

**ABSTRACT.** — A multivariate analytical approach was carried out in order to characterize travertine and «basaltina» which are the main building stones employed in the construction of Orvieto Cathedral. Results indicate the existence in the monument of three different lithotypes of «basaltina», «fine-grained», «coarse-grained» and «very fine-grained» distinguished on the basis of the size of leucite phenocrysts, and three distinct lithotypes of travertine, stromatolitic, phytohermal and detrital, distinguished on a textural basis.

The multivariate approach was a powerful tool in checking historical sources on the provenance of the materials. Comparisons between samples from the Cathedral and homologous samples from ancient quarries and zones of excavation revealed a provenance from a quite narrow zone, between Orvieto and Bagnoregio, for all lithotypes. Comparisons, between homologous samples from different zones in the Cathedral shows that the areas of excavation of «basaltina» and travertine did not change with time.

**RIASSUNTO.** — Un approccio analitico multivariato è stato sperimentato nella caratterizzazione del travertino e della «basaltina» in opera nel Duomo di Orvieto. I risultati ottenuti

evidenziano l'esistenza nel monumento di tre diverse litologie di «basaltina», definite «a grana fine», «a grana grossa» e «a grana molto fine» in base alla dimensione dei fenocristalli di leucite, e di tre litologie di travertino, stromatolitico, fitoermale e detritico, definite in funzione dei caratteri tessiturali.

L'approccio multivariato si è rivelato un potente mezzo nella verifica delle fonti storiografiche in merito alla provenienza dei materiali. Il confronto tra i campioni del Duomo e campioni omologhi prelevati da antiche cave e zone di estrazione ha dimostrato che tutti i litotipi provengono da un'area piuttosto ristretta situata tra Orvieto e Bagnoregio. Il confronto tra campioni omologhi prelevati da diverse zone del Duomo realizzate in epoche differenti ha invece evidenziato che le località di estrazione della «basaltina» e del travertino sono rimaste immutate nel tempo.

**KEY WORDS:** *Building stones, petrography, geochemistry, mineral chemistry, quarries, provenance, Orvieto Cathedral.*

### INTRODUCTION

Orvieto Cathedral is a masterpiece of Gothic Italian architecture. Like many contemporary monuments in Central Italy, it is characterized

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by a typical bichromy obtained using two different building materials: travertine and «basaltina», a local name for a leucite-bearing rock of tephritic to phonolitic composition. The external walls of the church and the circular windows of the apse are made of alternating «basaltina» and travertine blocks, and the inner walls of the apse and chapels of «basaltina» blocks only. Building of the Cathedral began in 1290 and lasted about three centuries. Therefore different zones of the Cathedral have different ages (fig. 1).

A large number of samples from the Cathedral and from ancient quarries were carefully characterized from the textural, chemical and mineralogical points of view (Moroni, 1991; Piasco, 1991; Querci, 1995; Giunchi, 1997) through a multivariate analytical approach. Results of the comparative examination of homologous samples from different zones in the monument and from quarries are reported in this work, with the aim of verifying the existence of any changes in the provenance of the materials used at different time and of interpreting the building events.

#### SAMPLING AND METHODS

A total number of about two hundred and fifty travertine and «basaltina» samples were taken from various zones inside and/or outside the church (fig. 1). They consist of cores and chips: cores were drawn by drill, chips were collected by hammer and chisel.

The method of sampling depended on the state of conservation, which is quite variable in the various zones of the monument: generalized ageing with cracking and exfoliation characterizes materials from outside, whereas very localized processes of exfoliation may be observed on the SSE rose window and upper wall inside the apse (Poli *et al.*, 1993; Moroni and Poli, 2000). In any case, deterioration mainly or exclusively involves «basaltina» and is due to physical or mechanical causes. Chips were taken from weathered material; cores represent sound material.

The historical data on provenance (Ricetti, 1988; Ricetti, *pers. comm.*, 1992) were checked by accurate geological and geomorphological study, then seventy fresh samples of travertine and «basaltina» were collected in outcrops from documented or recognizable ancient quarries. Exact identification of ancient quarrying sites was not so simple, since most of the place-names mentioned in the archives do not appear in present-day maps, so that in most cases samples were taken from different sites within suspected quarries; the criterion of macroscopical similarity with samples from the Cathedral was adopted in the choice of samples.

Most of the sampling sites lie in a quite narrow zone on the right bank of the Paglia river, between Orvieto and Bagnoregio, in the eastern part of the Vulsini volcanic area which belongs to the «Roman Magmatic Province» (Peccerillo and Manetti, 1985). Stratigraphy is characterized by two pyroclastic complexes with an interbedded ignimbrite formation (Faraone and Stoppa, 1989); the whole magmatic series lies on a Plio-Pleistocene sedimentary substratum. Distinct lava flows of variable extent alternate with tuffs in the pyroclastic complexes, together with small travertine lenses of lacustrine sedimentation. A few travertine samples were also collected in other localities mentioned in the historical sources as sites of provenance of building materials, such as Cetona and Titignano. The exact location of outcrop samples is shown in fig. 2.

All samples from the Cathedral and from outcrops were accurately characterized by optical microscopy, X-ray fluorescence spectroscopy (XRF) and scanning electron microscopy coupled with EDS microanalysis (SEM-EDS). XRF was performed on pelletized powdered samples, major elements (except MgO and Na<sub>2</sub>O, by atomic absorption) were determined by the full matrix correction method of Franzini and Leoni (1972) and trace elements following the Kaye's (1965) method. SEM-EDS microanalysis (15KV beam current, 60" count time) of clinopyroxene, plagioclase

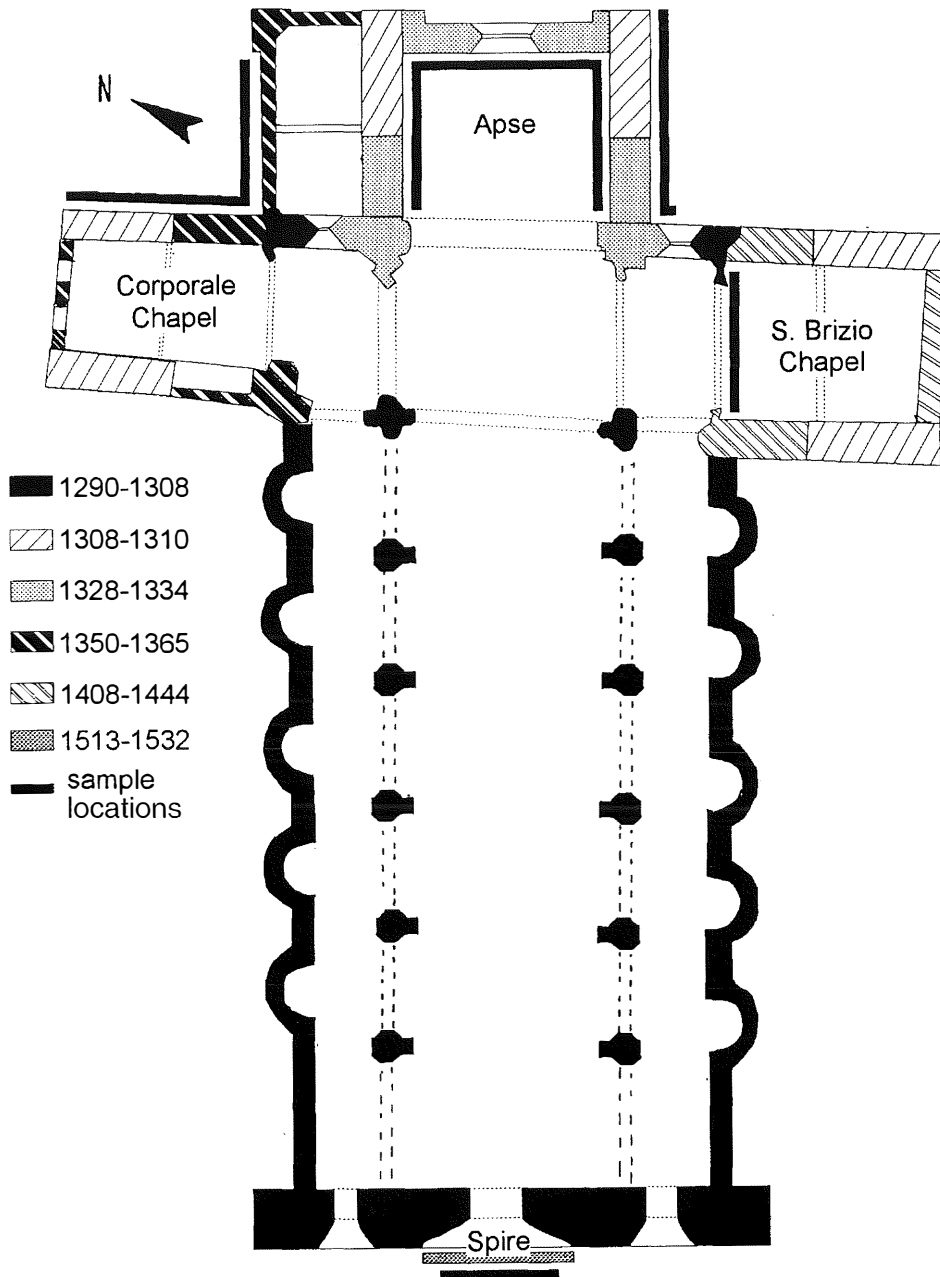


Fig. 1 – Chronological plan of Orvieto Cathedral, with sampling sites.

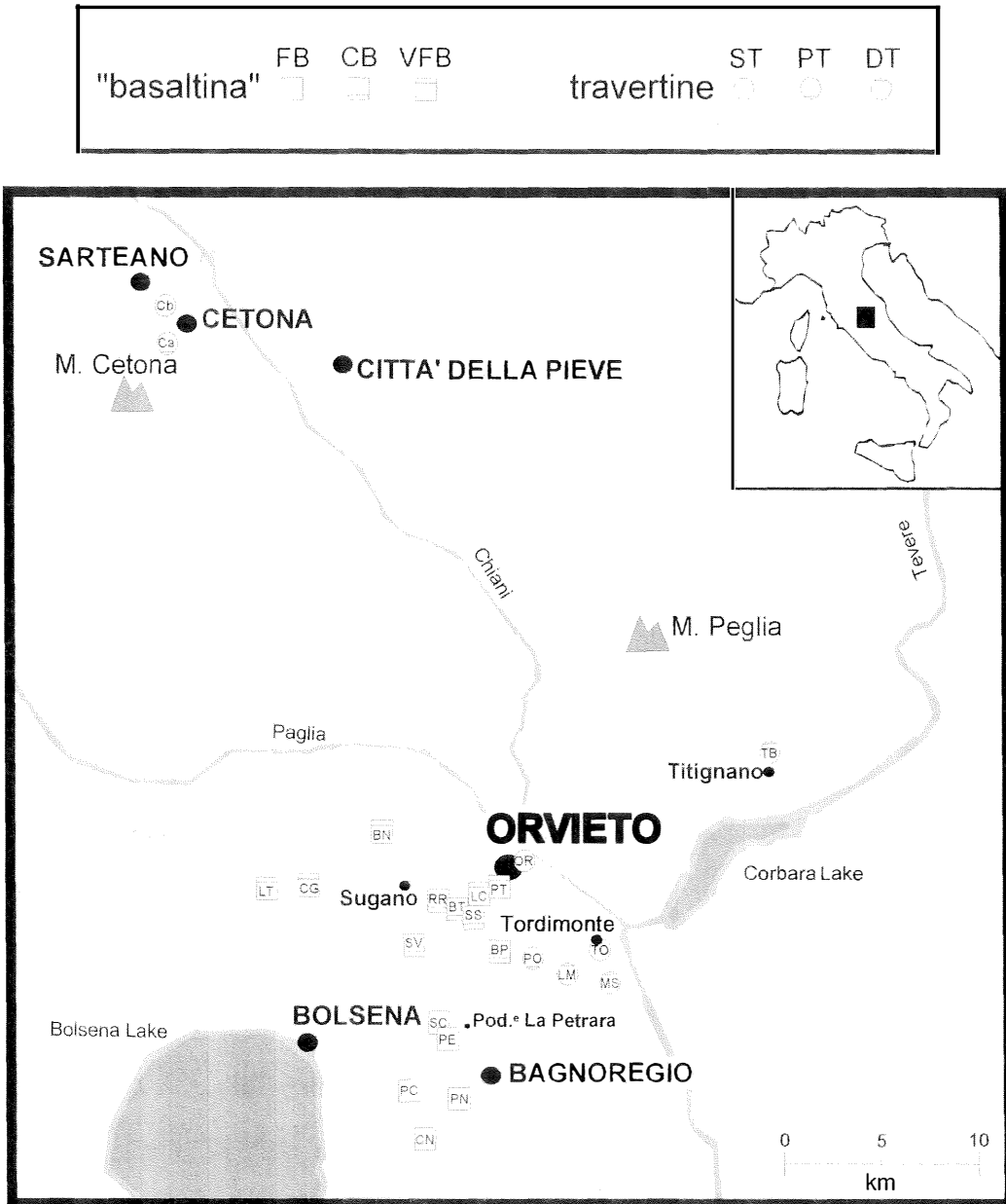


Fig. 2 – Sketch-map of studied area with location of sampling sites and corresponding lithologies. Phytothermal travertine was also sampled in Cb, and phytothermal and detrital travertine in TO (not shown, due to lack of space).

and Fe-ore was performed on polished thin sections obtained from samples, but only pyroxene analyses are reported in this work, for their greater archaeometric significance. A total number of about two hundred pyroxenes representative of the different lithologies and provenances were analysed. XRF and SEM-EDS data were treated by SIMCA multivariate statistical analysis (Bisani *et al.*, 1982a, b), a principal components analysis method in which empirical modeling is applied to a data matrix in order to group data into classes with different principal component values, giving information, on the structure of classes and relationships between data and classes.

## RESULTS

### «Basaltina»

*Petrography.* Three different lithologies of «basaltina» were recognized on a macroscopic scale: *i*) a grey, finely vesicular lava with white leucite phenocrysts about 2mm in size; *ii*) a darker, less vesicular and coarser-grained lithotype with rarer and larger leucite phenocrysts (about 10mm in size); *iii*) a dark, dense lava with no macroscopically visible leucite phenocrysts. Due to the size of the leucite phenocrysts, the lithotypes were named «fine-grained» (hereafter FB), «coarse-grained» (CB) and «very fine grained» (VFB), respectively. FB is the only constituent of the circular apse windows and the main component of the NNW Corporale Chapel and the SSE apse external walls; CB is the main constituent of the inner walls of the apse and the outer walls of the church; FB and CB are both constituents of the back of the spire; VFB is present as isolated blocks forming the inner wall of the S. Brizio Chapel and the SSE apse external wall.

Texture is porphyritic holocrystalline in all lithotypes from the Cathedral and from quarries, with leucite, clinopyroxene, plagioclase and spinel as phenocrysts and in the groundmass, and occasional biotite phenocrysts in some FB and CB samples (Table 1). Nevertheless, the smaller amount of

clinopyroxene and the presence of sanidine in CB suggest that it is more differentiated than FB, whereas the predominance of clinopyroxene in VFB is evidence of a less differentiated magma.

Clinopyroxene shows distinguishing features in the different lithologies. It is euhedral to subhedral, with irregular borders, pale to dark green in colour, sometimes with opaque inclusions and concentrically or sector-zoned in the FB and CB samples, but euhedral, with sharp edges, prismatic to acicular in shape, colourless or olive-green in colour in the VFB samples. Plagioclase is euhedral, frequently concentrically zoned with a cloudy core due to incipient sericitization. Leucite shows typical polysynthetic twinning and contains small clinopyroxene and opaque inclusions; it is generally fresh or mildly fractured.

Some FB and CB samples from the apse are characterized by typical alteration zones as iridescent cryptocrystalline aggregates affecting the fractures and borders of leucite crystals or the whole rock in the most altered samples.

*Mineral chemistry of clinopyroxenes.* The clinopyroxenes are diopsidic to salitic in composition (fig. 3). This is in general accordance with the mineral chemistry of potassic lavas from the Vulcini district (*e.g.* Holm, 1982). In particular, the colourless VFB clinopyroxenes are diopsidic, whereas all the other pale or dark green crystals show salitic composition. In the dark green pyroxenes, Al is much higher than in the colourless or pale green phases, and is positively correlated with Ti (fig. 4) and Fe<sup>2+</sup>. In the zoned crystals, rims are generally enriched in iron with respect to cores.

Clinopyroxenes from FB, CB and VFB samples show some distinguishing features: clinopyroxenes from FB form a quite large group containing the CB samples as a narrower group, whereas clinopyroxenes from VFB samples form two separate groups with different ranges of composition, depending on their diopsidic or salitic composition (fig. 3).

TABLE 1  
Summary of petrography of «basaltina».

Lithology	Provenance	Phenocrysts						Groundmass				
		Lc	Plag	Cpx	Fe-ore	San	Bi <sup>§</sup>	Lc	Plag	Cpx	Fe-ore	Bi
FB	Cathedral	****	***	****	**	**	*	****	****	**	***	
	PE (7)	****	***	***	**		*	****	****	**	***	
	SC (1)	****	*****	***	**			***	****	*	**	
	PC (1)	****	***	***	**	**		**	****	**	***	
	PN (1)	**	***	***	**		**	***	****	**	***	**
	CN (1)	**	***	***	**		**	*	****	**	***	
CB	Cathedral	****	***	**	*	**		**	****	**	***	
	RR (1)	****	***	**	*	**		***	****	**	***	
	SS (1)	****	***	**	*	**		**	****	**	***	
	BT (1)	***	**	**	**	*		***	***	**	***	
	SV (3)	****	***	**	*	**		***	***	**	***	
	BP (3)	****	***	***	*	**		**	****	***	***	
VFB	Cathedral	**	*	****	**			**	***	****	**	
	LC (1)	*	**	****	***			**	***	****	**	
	BN (4)	****	*	*				**	**	**	****	
	CG (2)	****	*	**	**			**	**	****	**	
	LT (1)	*	*	****				***	**	***	***	
	PT (2)	****	*	***	**			**	***	***	**	

<sup>§</sup>Mostly resorbed and represented by pseudomorphs of Fe-ore.

Abbreviations: Lc = leucite; Plag = plagioclase; Cpx = clinopyroxene; Fe-ore = opaque oxide; San = sanidine; Bi = biotite.

\* = trace; \*\* = minor; \*\*\* = abundant; \*\*\*\* = very abundant.

Number of samples from each quarry in brackets.

Data obtained through semiquantitative modal analysis.

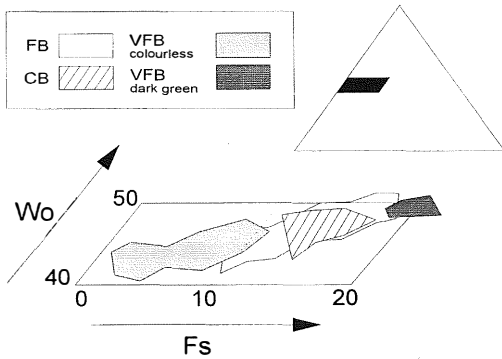


Fig. 3 – Composition of clinopyroxenes from «basaltina» in En-Fs-Wo system.

Pyroxenes from homologous lithologies in various parts of the Cathedral show similar features but different grades of similarity with their homologues from quarries (fig. 4).

**Geochemistry.** One hundred and twenty-six samples from the Cathedral and thirty samples from outcrops were analysed for major and trace elements. Data representative of the different lithologies and provenances are listed in Table 2.

According to Middlemost's (1975) classification, all the samples belong to the high-K series except those from the upper portion of the SSE apse inner wall, which belong to the K-series. These chemical compositions are in the general accordance with those reported in the literature for some leucite phonolites and leucite phonolitic tephrites from the Vulsini District (Holm *et al.*, 1982; Barton *et al.*, 1982; Rogers *et al.*, 1985).

From representative differentiation diagrams (fig. 5), it is evident that CB is more differentiated than FB, as it shows smaller amounts of ferromagnesian major and trace elements, and higher amounts of alkali, High Field Strength Elements (HFSE) and Large Ion Lithophile Elements (LILE) with respect to FB. VFB from the Cathedral shows chemical similarities with FB, whereas VFB from quarries is characterized by distinguishing features, such as higher CaO and ferromagnesian major and trace elements (Ni and Cr) amounts, and lower HFSE and LILE

contents with respect to the other lithotypes. Owing to these features it may be attributed to a less differentiated magma.

Scattering of data is generally quite small for the three lithologies and the ranges of variation of homologous samples from different zones in the church generally overlap. Nevertheless, among the CB samples, all those from the upper side of the SSE apse inner wall are clearly different from the others, with lower  $K_2O$  and higher  $Na_2O$  amounts. No other chemical differences can be observed; Rb, in particular, does not follow  $K_2O$  in its chemical behaviour, since it shows no significant variations among samples. SEM-EDS microanalysis of the alteration zones of leucite characterizing these samples revealed that they are anomalously enriched in Na and depleted in K with respect to sound leucite.

#### Travertine

**Petrography.** Most of the travertine samples of the Cathedral are «autochthonous» (Brancaccio *et al.*, 1986), as they were almost completely produced by biogenic processes of

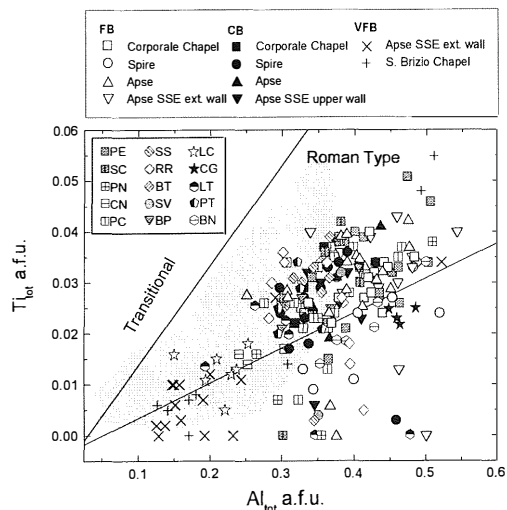


Fig. 4 – Mineral chemistry of clinopyroxenes from «basaltina». Partition lines and grey area are derived from literature data (Varekamp, 1980; Barton *et al.*, 1982; Holm, 1982; Conticelli *et al.*, 1991). Abbreviation: ext. = external.

TABLE 2

*Representative major (wt%) and trace element (ppm) analyses of «basaltina» samples from Orvieto Cathedral and from quarries.*

Sample	AB29	AB36	FA2	FA21	C110	B43	AB2	AB33	TQ23	TQ5	B	CN9
Lithotype	CB	CB	CB	CB	CB	CB	FB	FB	FB	FB	VFB	VFB
Location	Apse	Apse	Spire	Spire	Apse	Apse	Apse	Apse	Corp. Chapel	Corp. Chapel	S. Brizio Chapel	S. Brizio Chapel
					SSE u.w.	SSE u.w.						
SiO <sub>2</sub>	57.42	57.21	56.94	56.69	55.34	56.65	55.17	54.42	54.50	53.10	54.87	54.97
TiO <sub>2</sub>	0.52	0.53	0.42	0.52	0.50	0.48	0.57	0.58	0.48	0.51	0.59	0.57
Al <sub>2</sub> O <sub>3</sub>	19.98	19.62	20.20	20.40	19.78	19.67	19.74	20.48	20.98	20.64	18.53	18.63
ΣFe <sub>2</sub> O <sub>3</sub>	4.39	4.26	3.19	3.73	3.71	3.56	4.80	5.09	4.12	4.35	5.00	4.88
MnO	0.17	0.16	0.13	0.15	0.15	0.14	0.16	0.17	0.14	0.15	0.15	0.15
MgO	0.83	0.77	0.58	0.54	0.42	0.49	1.16	1.25	0.88	0.99	2.14	2.08
CaO	3.70	3.91	3.78	3.56	3.61	3.96	4.32	4.4	4.12	5.50	6.05	5.64
Na <sub>2</sub> O	3.39	3.49	3.18	3.00	5.85	4.82	2.92	2.55	2.41	2.75	2.59	2.52
K <sub>2</sub> O	8.04	7.68	9.42	7.86	6.93	8.30	7.74	8.25	8.71	7.45	8.26	8.62
P <sub>2</sub> O <sub>5</sub>	0.11	0.12	0.11	0.13	0.11	0.12	0.20	0.22	0.15	0.20	0.24	0.24
LOI	1.46	2.26	2.05	3.41	3.60	1.80	3.23	2.60	3.51	4.37	1.57	1.70
Total	100.01	100.01	100.00	99.99	100.00	99.99	100.01	100.01	100.00	100.01	99.99	100.00
Th	149	156	131	162	149	149	150	143	138	135	123	124
Pb	165	160	160	170	170	160	120	126	150	135	130	130
Ga	18	16	11	16	17	17	16	18	16	20	17	20
Rb	520	310	370	310	410	300	420	440	500	300	380	340
Sr	2100	2100	1700	2200	2100	2100	2100	2000	2000	2200	2000	1900
Y	25	28	24	39	29	35	29	28	41	37	36	35
Zr	620	660	420	700	640	610	560	550	530	530	550	540
Nb	40	45	22	46	43	43	39	37	39	38	39	38
Zn	82	88	71	81	78	72	83	82	83	81	90	91
Cu	32	240	52	16	8	17	12	25	14	20	31	56
Ni	15	11	9	8	16	8	8	10	26	10	35	27
Co	7	29	9	5	4	5	4	8	7	9	9	10
Cr	8	9	14	13	6	7	10	8	8	10	60	58
V	102	121	80	100	99	113	135	172	141	176	130	131
Ce	350	340	340	510	465	460	350	300	370	355	320	330
Ba	2400	2200	2500	2200	2000	2200	1900	1900	2100	1800	1700	1600
La	210	220	167	220	220	210	167	188	188	178	182	175

Precision is better than 5% for Rb, Sr, Zr, Ba, Th, La and Ce, and better than 10% for all other trace elements.

u.w., upper wall

e.w., external wall



TABLE 2, *continued*

Sample Lithotype Location	FA06 FB Spire	FA18 FB Spire	D186 FB Apse SSE e.w.	D220 FB Apse SSE e.w.	RR CB Quarry	SV1 CB Quarry	PN FB Quarry	CN FB Quarry	PE FB Quarry	BN1 VFB Quarry	LT VFB Quarry	LC VFB Quarry
SiO <sub>2</sub>	53.52	54.86	55.75	55.41	56.85	56.05	58.16	57.81	56.48	50.29	48.85	50.25
TiO <sub>2</sub>	0.54	0.54	0.54	0.54	0.51	0.47	0.64	0.61	0.54	0.77	0.78	0.95
Al <sub>2</sub> O <sub>3</sub>	19.50	19.92	19.92	19.89	20.28	20.24	19.34	19.01	21.23	19.50	18.02	18.75
ΣFe <sub>2</sub> O <sub>3</sub>	4.63	4.75	4.54	4.66	3.66	3.62	4.64	4.60	4.40	7.72	7.64	8.00
MnO	0.16	0.16	0.16	0.15	0.14	0.14	0.12	0.12	0.15	0.16	0.15	0.15
MgO	0.98	1.00	0.79	0.85	0.77	0.60	1.60	1.27	1.08	2.50	4.77	3.96
CaO	5.90	4.48	4.62	4.92	3.68	3.32	4.24	4.12	4.51	7.75	9.90	8.92
Na <sub>2</sub> O	2.74	2.93	2.69	2.97	3.04	2.90	2.77	2.31	2.50	1.95	1.39	1.64
K <sub>2</sub> O	7.38	7.93	7.09	6.56	9.16	9.66	7.55	8.64	7.99	7.95	6.96	6.01
P <sub>2</sub> O <sub>5</sub>	0.24	0.24	0.20	0.21	0.11	0.09	0.32	0.25	0.18	0.41	0.40	0.39
LOI	4.42	3.20	3.70	3.84	1.80	2.92	0.62	1.26	0.94	0.99	1.14	0.98
Total	100.01	100.01	100.00	100.00	100.00	100.01	100.00	100.00	100.00	99.99	100.00	100.00
Th	133	139	127	132	167	148	68	77	156	68	51	41
Pb	144	130	204	170	164	160	66	75	122	55	44	45
Ga	17	20	16	19	17	16	20	20	21	18	17	19
Rb	320	370	320	370	330	330	520	490	350	390	460	370
Sr	2100	2100	2000	2000	2200	2000	1100	1100	2100	1600	1500	1300
Y	24	29	27	26	32	40	27	36	27	37	35	32
Zr	550	560	530	520	670	620	450	410	560	340	290	300
Nb	37	38	40	35	45	44	22	23	38	21	16	16
Zn	83	79	96	85	78	80	60	70	77	92	77	89
Cu	17	15	21	15	11	17	5	11	12	22	45	28
Ni	5	11	16	18	11	15	13	20	10	27	61	32
Co	6	6	4	10	3	4	10	9	7	23	25	23
Cr	16	16	13	10	9	0	7	3	9	10	63	23
V	154	169	150	160	103	121	100	119	166	215	224	201
Ce	370	420	410	380	350	450	230	250	290	240	200	200
Ba	1900	1900	1800	1900	2400	2300	1200	1200	1900	1400	1300	1250
La	165	170	177	171	220	200	131	121	181	128	108	105

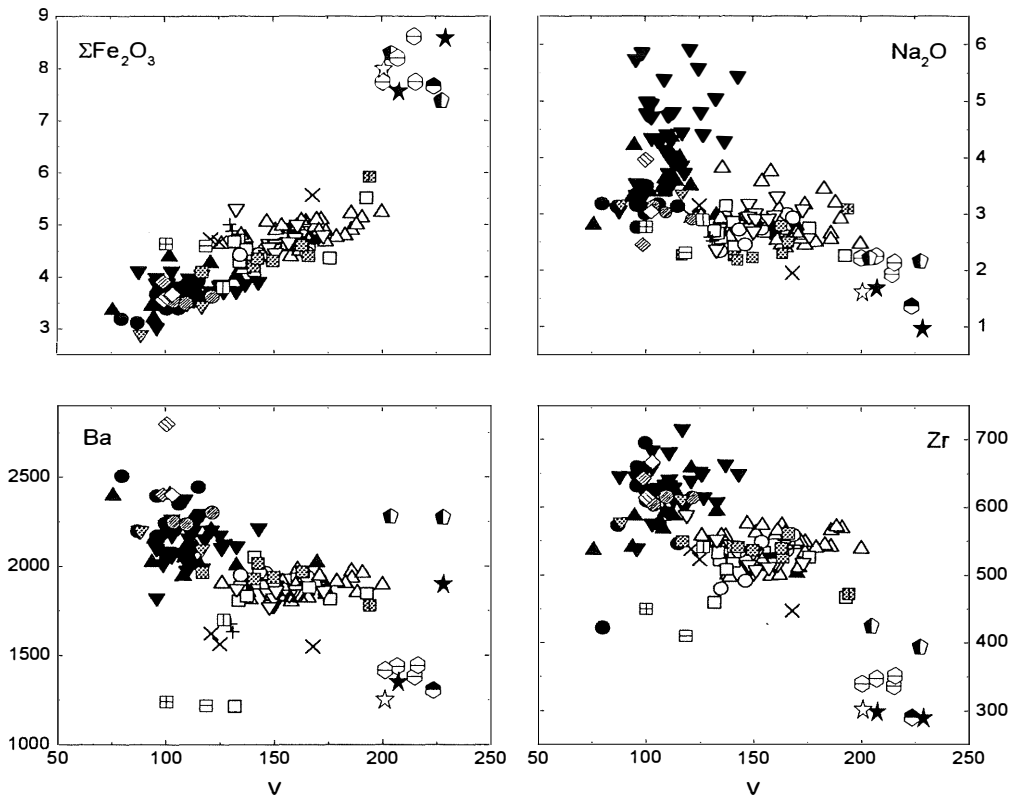


Fig. 5 – Representative major and trace elements versus V for «basaltina» samples. Symbols as in fig. 4.

calcium carbonate encrustation involving macro- and microphyta in growth position; they consist of stromatolitic and phytohermal travertines. Stromatolitic travertines (hereafter ST) derive from chemical encrustation by fibrous calcite of algal felts, giving rise to oncoidal or concentric structures. Phytohermal travertines (PT) derive from carbonatic encrustation of microphyta (Bryophyta and Tallophyta felts) and macrophyta (hygrophyte stalks).

A small number of samples belong to detrital travertines (DT), as they are composed of biogenically encrusted phyto- and bioclasts. They may be divided in to two different groups: phyto-bioclastic travertines and travertinous sands. Phyto-bioclastic travertines are formed by vegetal and faunal fragments

arenitic in size, linked together by biogenic calcite encrustations due to the biological activity of cyanophyta and bacteria biocenosis. Travertinous sands are exclusively formed from small rounded calcite grains.

Faunal contents are not abundant in all the travertines and are mainly represented by rare Ostracoda and freshwater Gastropoda. Isolated Characeae oogonia were also found in some stromatolitic travertines. Instead, most of the samples are characterized by a siliciclastic component dispersed in the carbonatic matrix or concentrated in small aggregates. It consists of quartz, alkali-feldspar, white mica, pyroxene, biotite, epidote, titanite and chlorite crystals or mineral clasts, together with rare tuff or lava fragments. Some minerals, such as quartz, alkali-feldspars and white mica, may be

TABLE 3  
Summary of the petrography of travertine.

	Cathedral	TO	TB	Ca	Cb	OR	PO	LM	Ms
ST		5	—	—	2	5	—	—	—
f.c.	(Ostracoda, Gastropoda, Characeae oogonia)	(Characeae ogonia, Ostracoda)			—	(Gastropoda)			
s.c.	(Qz, K-fld, Bi, Cpx, MS)	(Qz, Cpx, K-Fld, Bi, Chl)			—	(Qz, K-fld, Cpx, PI, Pyr)			
PT		8	—	2	3	—	5	—	—
f.c.	(Ostracoda, Gastrpododa)	(Ostracoda, Gastropoda)		(Ostracoda, Gastropoda)	—		—		
s.c.	Cpx, Qz, K-fld (Ti, Chl, PI, Ep)	Qz, PI, Cpx, (Bi,K-fld, Ep, Ti, Chl, Pyr)		Qz (K-fld, Ms, Chl)	—		(Qz, CPx, Pyr)		
DT		2	1	—	—	—	—	2	3
f.c.	Ostracoda, Gastropoda	(Ostracoda, Gastropoda)	(Ostracoda)	(Ostracoda)	(Ostracoda)				
s.c.	Cpx, Bi, K-fld		(Qz, Ms)					(Cpx, Pyr)	(Cpx, Pyr, Qz, Pl)

f.c. = fossil component; s.c. = siliciclastic component; numbers refer to number of samples; ( ) rare; — not present.

Abbreviations: Qz = quartz; K-fld = alkali-feldspar; Bi = biotite; Cpx = clinopyroxene; Ti = titanite; Chl = chlorite; PI = plagioclase; Ep = epidote; Ms = muscovite; Pyr = pyroclastic fragments.

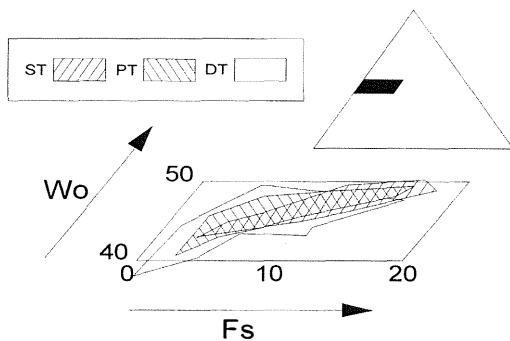


Fig. 6 – Composition of clinopyroxenes from travertine in En-Fs-Wo system.

genetically related to sedimentary processes, whereas all the other minerals may be directly or indirectly related to magmatic processes.

The siliciclastic component is generally more abundant in phytohermal and detrital than in stromatolitic travertines. Magmatic phases are particularly abundant in PT samples from the NNW Corporale Chapel wall and DT samples from the SSE apse external wall. The sedimentary fraction (dominated by quartz) is the main constituent of ST samples from the apse, S. Brizio Chapel and the spire, whereas mixed magmatic (chlorite, biotite) and sedimentary (quartz, alkali-feldspar) components are characteristic of the rest of the samples. The mineral phases, with dimensions in the range 10-200 $\mu$ m, maintain their habitus and have sharp edges.

The three different lithologies are not equally distributed in the different parts of the Cathedral: ST is the most representative lithology in the walls of the apse and the external back of the spire; PT is the main constituent of the external NNW wall of the Corporale Chapel; DT is mainly represented in the external SSE wall of the apse; ST and DT are equally represented in the S. Brizio Chapel.

The quarry samples show a wide range of textures with variable abundances and composition of siliciclastic and fossil components. The textural features of the Cathedral and quarry samples are listed in Table 3.

**Mineral chemistry of clinopyroxenes.** The clinopyroxenes are diopsidic to salitic in composition and their ranges of variability in the three lithologies from both Cathedral and quarries largely overlap (figs. 6 and 7). They also show great similarities with representative samples from the Vulsini District, reported in the literature (Barton *et al.*, 1982; Conticelli *et al.*, 1991).

**Geochemistry.** Seventy samples from the Cathedral and thirty-eight samples from outcrops were analysed for major and trace elements. Data representative of the different lithologies and provenances are listed in Table 4.

Insoluble residue (I.R. in fig. 8) is in positive correlation with SiO<sub>2</sub> in all samples, but the ST samples from the apse, spire and S. Brizio Chapel show no correlation between SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> amounts (fig. 8). This is in good agreement with the mineralogical composition of the siliciclastic fraction, which is dominated by quartz.

The ranges of variation of the chemical compositions are quite different in the three lithotypes: PT is characterised by higher

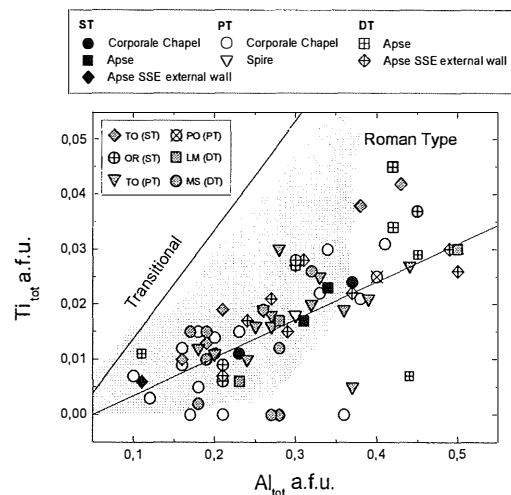


Fig. 7 – Mineral chemistry of clinopyroxenes from travertine. Partition lines and grey area are derived from literature data (Varekamp, 1980; Barton *et al.*, 1982; Holm, 1982; Conticelli *et al.*, 1991).

TABLE 4

Data on representative major (wt%) and trace element (ppm) analyses and insoluble residue (I.R., wt%) of travertine samples from Orvieto Cathedral and from quarry.

Sample	AB15	TQ25	TQ24	A15	A4	CN6	CN7	D166	D208	FA59	FA62	OR1	P02	TO1d	TO2a	TO2
Lithotype	PT	PT	ST	ST	DT	ST	DT	ST	DT	PT	ST	ST	PT	PT	ST	DT
Location	Apse	Corp.	Corp.	Chapel	Apse	S. Brizio	S. Brizio	Chapel	Chapel	Spire SSE e.w.	Spire SSE e.w.	Quarry	Quarry	Quarry	Quarry	Quarry
SiO <sub>2</sub>	11.35	11.32	4.60	4.15	10.17	4.07	1.74	5.40	7.37	13.86	3.15	6.47	2.63	8.23	3.55	1.86
TiO <sub>2</sub>	0.05	0.04	0.01	0.01	0.03	0.01	0.00	0.03	0.03	0.01	0.00	0.05	0.01	0.10	0.02	0.00
Al <sub>2</sub> O <sub>3</sub>	1.54	1.14	0.30	0.31	0.73	0.33	0.39	0.96	0.89	0.22	0.33	1.58	0.39	2.21	0.41	0.12
ΣFe <sub>2</sub> O <sub>3</sub>	0.92	0.40	0.11	0.14	0.31	0.11	0.17	0.32	0.31	0.12	0.08	0.58	0.20	0.84	0.17	0.13
MgO	n.d.	0.54	0.76	0.85	0.70	n.d.	n.d.	1.00	0.98	0.67	0.72	0.55	0.46	0.90	0.72	n.d.
CaO	45.77	46.97	51.44	51.45	47.27	51.99	55.03	50.01	48.34	45.22	51.90	48.39	53.27	47.22	52.01	53.84
Na <sub>2</sub> O	n.d.	0.26	0.08	0.20	0.10	n.d.	n.d.	0.04	0.20	0.10	0.10	0.21	0.11	0.10	0.14	n.d.
K <sub>2</sub> O	0.29	0.40	0.07	0.22	0.32	0.03	0.02	0.27	0.30	0.09	0.21	0.44	0.10	0.48	0.13	0.02
P <sub>2</sub> O <sub>5</sub>	n.d.	0.17	0.18	0.62	0.53	n.d.	n.d.	0.60	0.66	0.17	0.17	0.27	0.24	0.22	0.16	n.d.
LOI	40.05	38.74	42.41	42.00	39.80	43.45	42.64	41.32	40.84	39.52	43.29	41.43	42.50	39.67	42.68	44.02
Total	100.00	99.98	99.96	99.95	99.96	99.98	99.99	99.95	99.92	99.98	99.95	99.97	99.91	99.97	99.99	99.99
I.R.	13	14	4.9	3.1	9.5	4.4	2.1	4.9	6.2	n.d.	3.8	11	3.3	12	4.5	2
Sr	1120	1320	1810	2220	1180	1960	2120	1680	2020	1060	2350	1650	1730	1250	1660	1710
Ba	1040	97	49	24	86	220	147	55	65	33	165	188	69	161	65	61
Mn	290	300	400	500	400	200	80	600	700	300	400	300	800	400	200	80
Zn	17	21	28	22	12	3	2	28	34	19	26	29	34	24	18	3
Rb	n.d.	40	5	3	18	n.d.	n.d.	12	9	7	16	40	16	44	9	n.d.
Zr	n.d.	56	42	42	37	n.d.	n.d.	54	52	33	47	66	41	65	41	n.d.
La	n.d.	14	14	11	8	n.d.	n.d.	2	10	10	7	19	12	16	13	n.d.
Cu	n.d.	17	15	14	13	n.d.	n.d.	16	19	17	17	20	19	23	19	n.d.
Pb	n.d.	9	6	2	19	n.d.	n.d.	16	22	33	8	13	8	15	5	n.d.
Ce	n.d.	2	2	3	5	n.d.	n.d.	8	4	2	2	10	17	10	2	n.d.

Insoluble residue measured by gravimetry. Precision is better than 5% for Sr, Ba and Mn, and better than 10% for I.R. and the other trace elements. n.d., not determined. e.w., external wall.

insoluble residue and lower MgO and Sr contents with respect to ST. The range of variation of PT also lies in a much more restricted zone with respect to ST. DT may be divided in two groups, the former lying within

the ST, and the latter within the PT range of variation or in a separate zone in the case of some elements such as Sr (fig. 8).

Homologous samples from different parts of the Cathedral are quite similar; in particular,

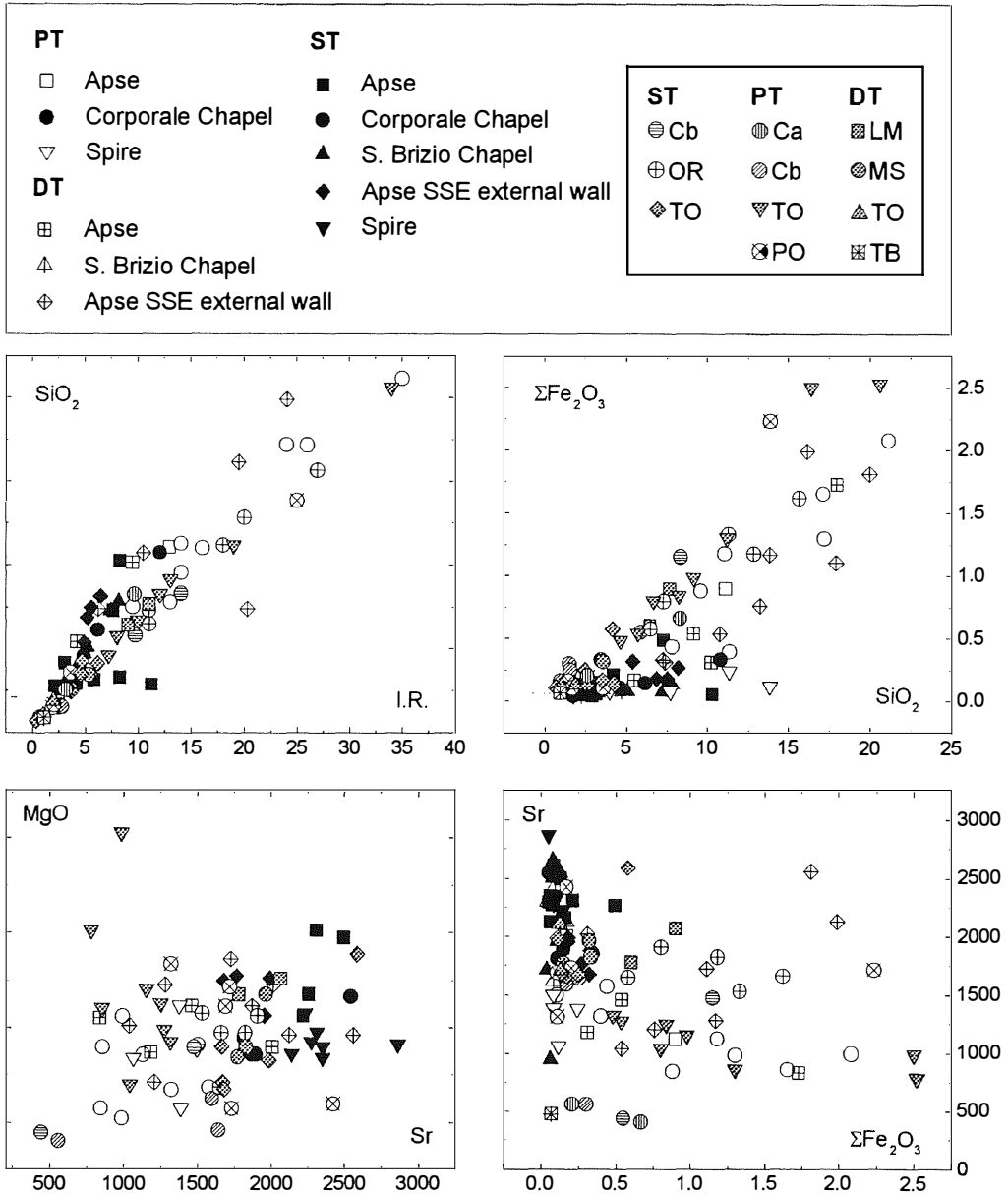


Fig. 8 – Variation diagrams of representative major and trace elements for travertine samples.

PT from the NNW Corporale Chapel external wall covers a wide range containing all the other groups of samples; ST samples completely overlap, except those from the spire which form a distinct group for some elements; DT samples generally completely overlap except those from the SSE apse external wall and the inner S. Brizio wall, which form separate groups for some elements.

Among the outcrop samples, only TO lithologies show some similarities with their homologous ST, PT and DT samples from the Cathedral, although their ranges of variation do not completely overlap those of the samples from the monument.

## DISCUSSION

### *Provenance of «basaltina»*

The results point to the existence of three different lithotypes of «basaltina», named «fine-grained» (FB), «coarse-grained» (CB) and «very fine-grained» (VFB), in the Cathedral. In spite of their mutual differences, these lithotypes may all be related to the Eastern Vulsini magmatic activity, well evidenced by whole-rock geochemical features and the mineral chemistry of clinopyroxenes.

The three groups are characterized by very different textural and geochemical features. VFB is also clearly distinguishable from the mineral chemistry point of view, since most of the pyroxenes form a distinct group with typical geochemical features. Whole-rock and clinopyroxene geochemical data are shown in fig. 9.

Looking at these points, it is possible to discriminate among possible sources as deduced from historical information. Only PE samples from La Petrara, a farm about 3km NW of Bagnoregio, show close textural and chemical similarities with the FB samples from the Cathedral. Among the other FB outcrop samples, SC and PC are chemically similar, but quite different texturally, whereas PN and CN have no similarities with the samples from the Cathedral.

The quarry at La Petrara, which is mentioned in archive documents, has a small extraction face about 30m wide where «basaltina» forms a lens set in tuff levels, so that it did not provide large amounts of stone. These amounts, however, are consistent with the relatively small volume of stone employed in the Cathedral, so that the quarry may be considered as the only source of FB.

As regards CB, the textural and chemical features show a provenance from a small area on the outskirts of Orvieto where small «basaltina» lenses with very peculiar features («Sugano leucitifero»; Jacobacci *et al.*, 1970) outcrop. All the outcrop samples from this area approximate those from the Cathedral. In particular, RR and SS show the best textural similarities, whereas all the CB outcrop samples have total-rock and pyroxene chemistry data spreading over the range of variability of the samples from the Cathedral.

Looking at these points, no clear distinction may be made among the possible sites of extraction of CB. However, based on historical information on provenance, and on considerations on the proximity and practicability of the quarries, we may restrict the source area of CB to sites on the outskirts of Orvieto, where the RR and SS samples were collected. In particular, a large ancient quarry front in the sampling site of RR is clear evidence of intense quarrying in the past.

The provenance of VFB cannot be established since the lithofacies from the areas selected on historical basis, although similar to VFB from the Cathedral on a macroscopic scale, are very different from the textural and chemical points of view. However, the material was certainly extracted in this part of the Vulsini District, as evidenced by the mineral chemistry of clinopyroxenes. In particular, the clinopyroxenes from one of the samples (LC) show some chemical similarities with those of the samples from the Cathedral, so they may be related to the same magma source but with a different degree of evolution.

Based on these assumptions, the provenance of VFB was checked in another area not

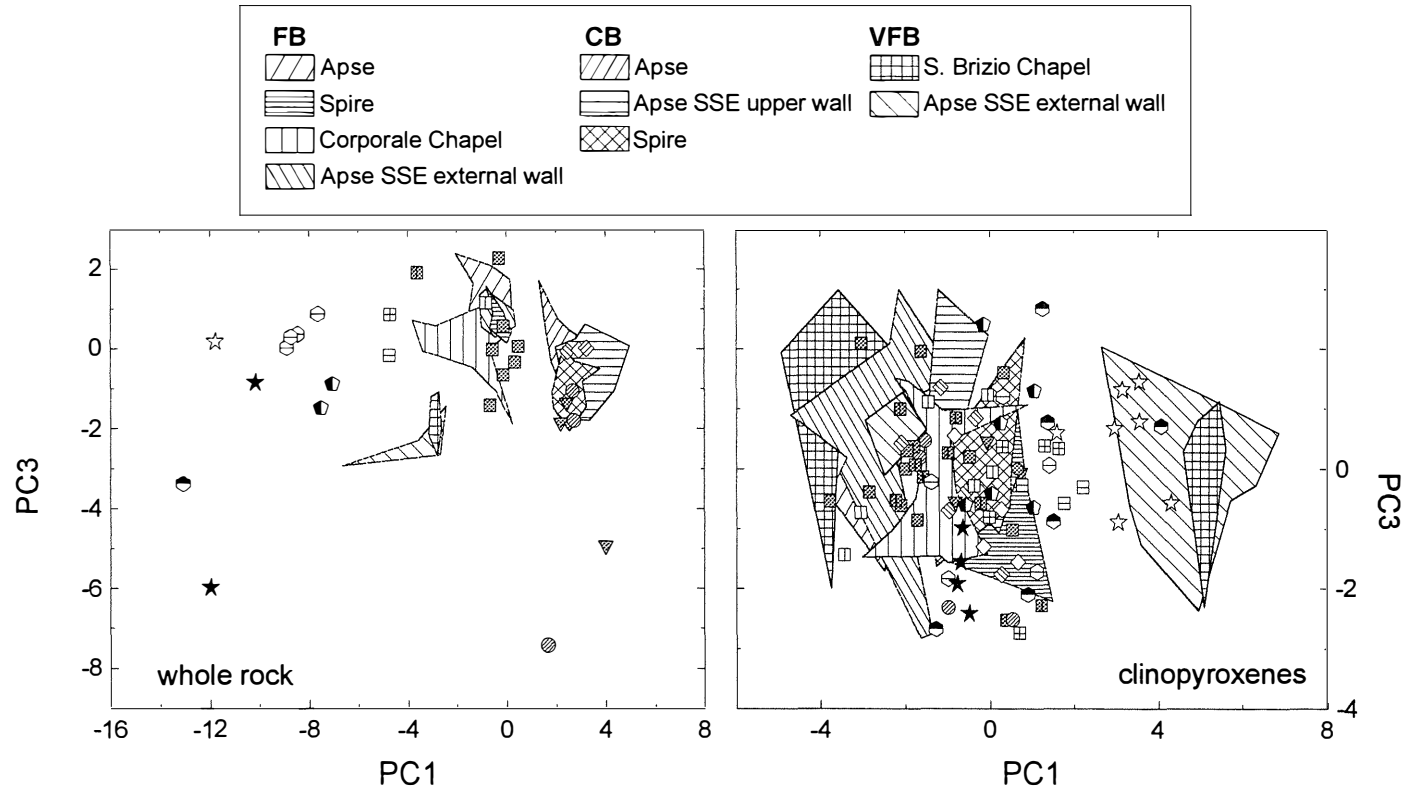


Fig. 9 – Provenance of FB, CB and VFB as exemplified by principal component (PC1, PC3) statistical plots. Symbols of quarry samples as in fig. 4.



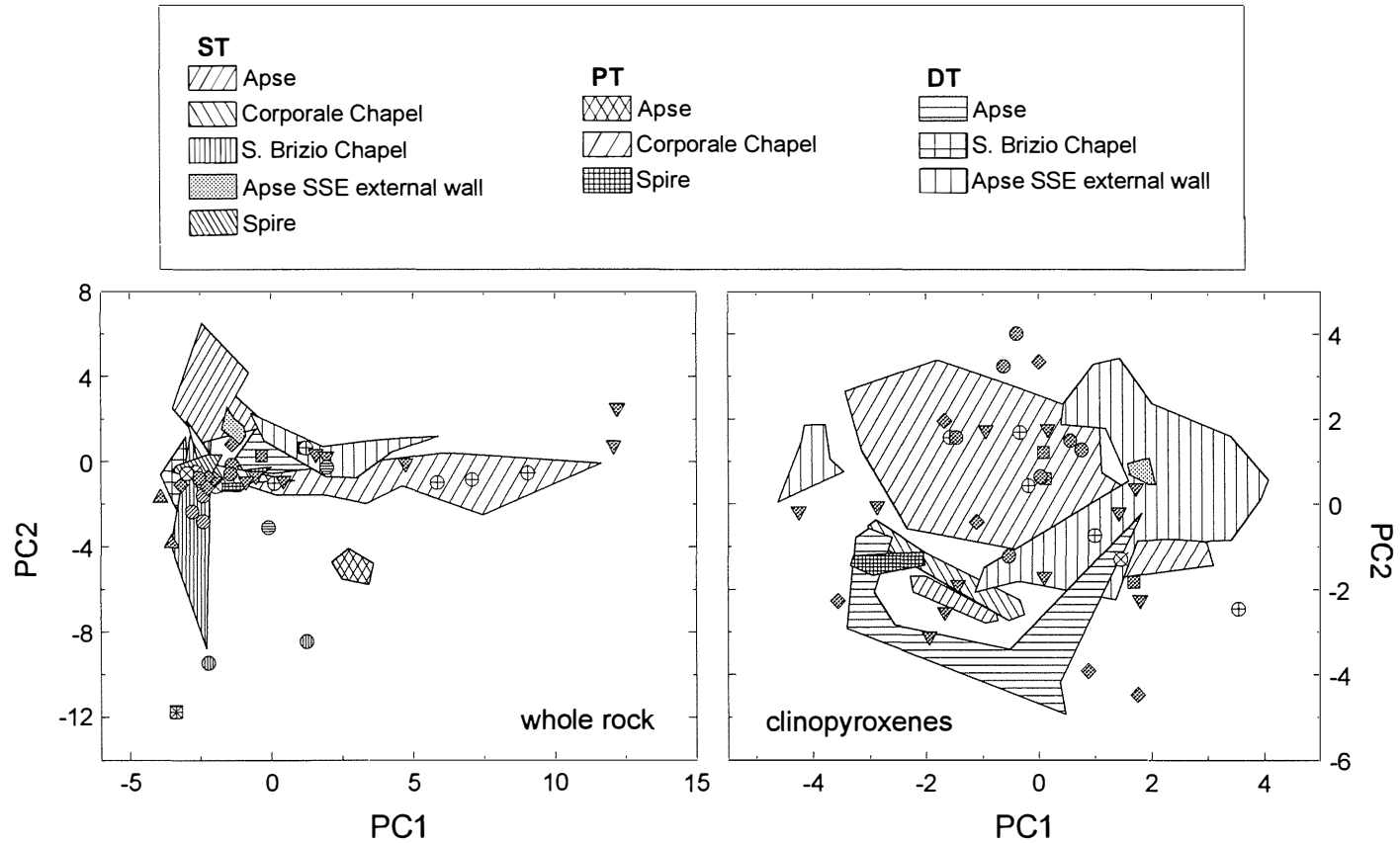


Fig. 10 – Provenance of ST, PT and DT as exemplified by principal component (PC1, PC3) statistical plots. Symbols of quarry samples as in fig. 8.

specifically mentioned in the historical sources, located in the outskirts of Orvieto, about 2 km W of the town, where tephrite leucitites belonging to the «Lower Pyroclastic Complex» outcrop.

No significant differences can be found between homologous samples from different parts of the Cathedral (fig. 9), except for a considerable discrepancy in all the CB samples from the upper SSE wall of the apse, and for some FB samples from the SSE window and external wall of the apse. These samples show diffuse exfoliation processes on a macroscopic scale, and alteration zones developing within the leucite grains on a microscopic scale. They also have anomalous  $\text{Na}_2\text{O}/\text{K}_2\text{O}$  ratios but no significantly different Rb values with respect to sound material. According to the observations of Quantin and Lorenzoni (1992) and Putnis *et al.* (1994), the weathering process is a ion-exchange analcimization of leucite. The relatively higher Rb contents are due to the fact that Rb substitutes K in leucite but not Na in analcime; therefore they are inherited from the original leucite.

The question whether analcimization was pre-existent to quarrying or subsequent to the construction of the building can be resolved if it is considered that analcimization is generally inherited from hydrothermal processes in which Na-rich fluids at suitable temperatures can promote ion-exchange processes in potassic magmatic rocks (Quantin and Lorenzoni, 1992). Analcimization also involves both FB and CB from different locations inside or outside the apse. Therefore, the material was already analcimized in the quarry before extraction and use. The site of excavation of this material cannot be specified because our strategy was to reject altered material during sampling from outcrops.

#### *Provenance of travertine*

Results indicate the existence of three different lithotypes of travertine, stromatolitic (ST), phytohermal (PT) and detrital (DT), employed in building the Cathedral. The textural and compositional features, particularly

the presence of typical organic (fossils of Gastropoda, Ostracoda and Characeae) and inorganic (magmatic rock and mineral fragments) components, suggest that sedimentation of these travertines occurred in a lacustrine basin near a volcanic area.

A lake was probably a complex anastomosing system whose margins were sites of algal bioherms or bacterioherms giving rise to stromatolitic travertines (Ford and Pedley, 1996), whereas the interior of the basin, poorly drained slopes or marshy areas were sites of sedimentation of phytohermal and, locally, phytoclastic travertines and travertinous sands (D'Argenio and Ferreri, 1988). Remains of plants, animals and remnants of bacterial activity within the samples is clear evidence that calcium carbonate precipitation occurred in a cool water regime, so it is better to use the term «tufa» to describe all these lithologies (Pedley, 1990). The characteristics of the magmatic component, particularly the tuff and lava fragments within the travertine, indicate lithoclast derivation from weathering processes involving pyroclastic and lava formations; transport of the epiclastic component was limited, as indicated by the angularity of the clasts, therefore their provenance is probably very close to the travertine depositional environment.

These features are consistent with the geological setting of the Vulsini District near Orvieto, where Pleistocene lacustrine sedimentation during periods of suspension of volcanic activity is documented (Varekamp, 1980). For the same reason, more distant places mentioned in the historical sources, such as Cetona and Titignano (samples Ca, Cb and TB) are to be rejected as sites of extraction of travertine. No magmatic events before or during travertine deposition are documented in these areas to justify the presence of the magmatic component in the travertines (Jacobacci *et al.*, 1967, 1970). In addition, the mineral chemistry of clinopyroxenes is a typical feature of the eastern part of the Vulsini District.

The fact that Cetona and Titignano did not

provide the travertine for the Cathedral is not in contrast with the intrinsic validity of the historical sources, since the exact lithology of materials from each quarry is not specified in the documents. Therefore, they were sites of provenance or collection of other construction materials also employed in the building site. Titignano, in particular, was an important port in the past for the transport of goods along the Tiber to and from Rome.

Among the samples from the outskirts of Orvieto, those from Tordimonte (TO) and its surroundings (LM, MS) show the best textural and chemical similarities with the materials from the Cathedral (Table 3; fig. 10). The stromatolitic OR and phytohermal PO samples do not show the same abundance and/or variety of the siliciclastic component with respect to their homologues from the Cathedral, and OR shows chemical similarities with phytohermal rather than stromatolitic travertine. Moreover, the three lithotypes ST, PT and DT all outcrop close to each other within the same areas containing evidence of extensive quarrying in the past.

No significant differences can be found between homologous samples from different parts of the Cathedral (fig. 10), so that the area of extraction was probably the same in the various building phases.

#### CONCLUSIONS

Archaeometric characterization of the materials employed in the construction of Orvieto Cathedral confirmed and partly clarified the validity of historical data on provenance and building events. As regards provenance, it was possible to identify the area of extraction as the zone between Orvieto and Bagnoregio. In particular, among the three lithotypes of «basaltina», FB came from the same quarry located a few kilometres NW of Bagnoregio, whereas CB came from the «leucitofiro» lava lenses outcropping slightly SW of Orvieto. Instead, the area of extraction of VFB was not clearly determined, but was

probably located a few kilometers W of Orvieto; travertine was extracted near Tordimonte. The exact location of the CB, VFB and travertine quarries will be the subject of a future work concerning detailed characterization of the materials in the sites of extraction.

The obtained results are in partial accordance with historical information about provenance (Ricetti, 1988) as they confirm some localities as sites of extraction, but exclude others for the provenance of travertine and «basaltina». This is a consequence of the general difficulty in locating ancient quarries, due to the fact that most of the place-names mentioned in archive documents do not appear in the present-day maps. It also depends on the fact that the exact lithology of the materials from each quarry is not specified in the documents. Correct attribution of the source areas for building materials may be possible after accurate characterization of the number of lithic materials employed in the construction and decoration of the Cathedral.

Comparisons between homologous samples from different parts in the Cathedral indicate that «basaltina» and travertine quarries did not change over time. That is in contrast with the hypothesis of a progressive displacement of the extraction sites with time formulated by historians (Ricetti, *pers. comm.*, 1992).

In the light of these points, the variability observed in the travertine and «basaltina» reflects the intraformational variability of the lithotypes. However, an additional contribution may be ascribed to re-mixing of blocks after quarrying. Storing of materials in quarries or building sites was a common practice in the Middle Ages, and re-use of blocks after demolition in the reconstruction of some parts of the Cathedral, such as the apse (1335) and S. Brizio Chapel (1408-1444), is documented.

The results of this work provide an important contribution to reconstruction of the «history» of Orvieto Cathedral by furnishing a scientific basis to the interpretation of historical documents on provenance, and to the creation of a chronological map of the sites of

extraction of the materials employed in building such an important monument. Our future aim is complete knowledge of the building phases of the church through characterization of the materials employed in other parts of the monument.

#### ACKNOWLEDGMENTS

We thank the «Soprintendenza per i Beni Ambientali, Architettonici, Artistici e Storici dell'Umbria» for generous assistance during sampling in Orvieto Cathedral. We are also grateful to Danilo Chiocchini for his precious support in SIMCA analysis. Research was supported by C.N.R. of Italy (Comitato per la Scienza e la Tecnologia dei Beni Culturali).

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