Sedimentary Zeolite Deposits in Italy
Part 1: Campania

Introduction:

Two important zeolitized volcaniclastic units, linked to the volcanic activity of Campi Flegrei (*Phlaegrean Fields*), occur in Campania region (South Italy): **Campanian Ignimbrite** (CI) and **Neapolitan Yellow Tuff** (NYT).

Campi Flegrei are a volcanic district, including Campi Flegrei, *sensu stricto*, the town of Naples, the volcanic islands of Procida and Ischia and the north-western part of Naples Gulf (Fig. 1).

Data concerning the beginning of the volcanic activity in this area of the Campania region are uncertain as the only available information derives from some deep drillings, which encountered volcanic rocks dated at about 2 My. The oldest outcropping rocks, on the contrary, date back to some 60 ky. The most important eruptive events of this volcanic field, which were responsible for the emplacement of the CI and the NYT, occurred at 39 ky and at 15 ky, respectively. Each event caused the formation of a caldera. The first one gave rise to the sinking of a wide area including Campi Flegrei, a part of the Naples town and a portion of the Naples and Pozzuoli bays. The second one originated a sinking of an area including a part of Campi Flegrei and of the Pozzuoli bay. After the NYT eruption the area experienced many eruptive events followed by periods of inactivity, until 1538 A.D. with the eruption of Monte Nuovo, the most recent volcano in Europe (1).

CAMPANIAN IGNIMBRITE

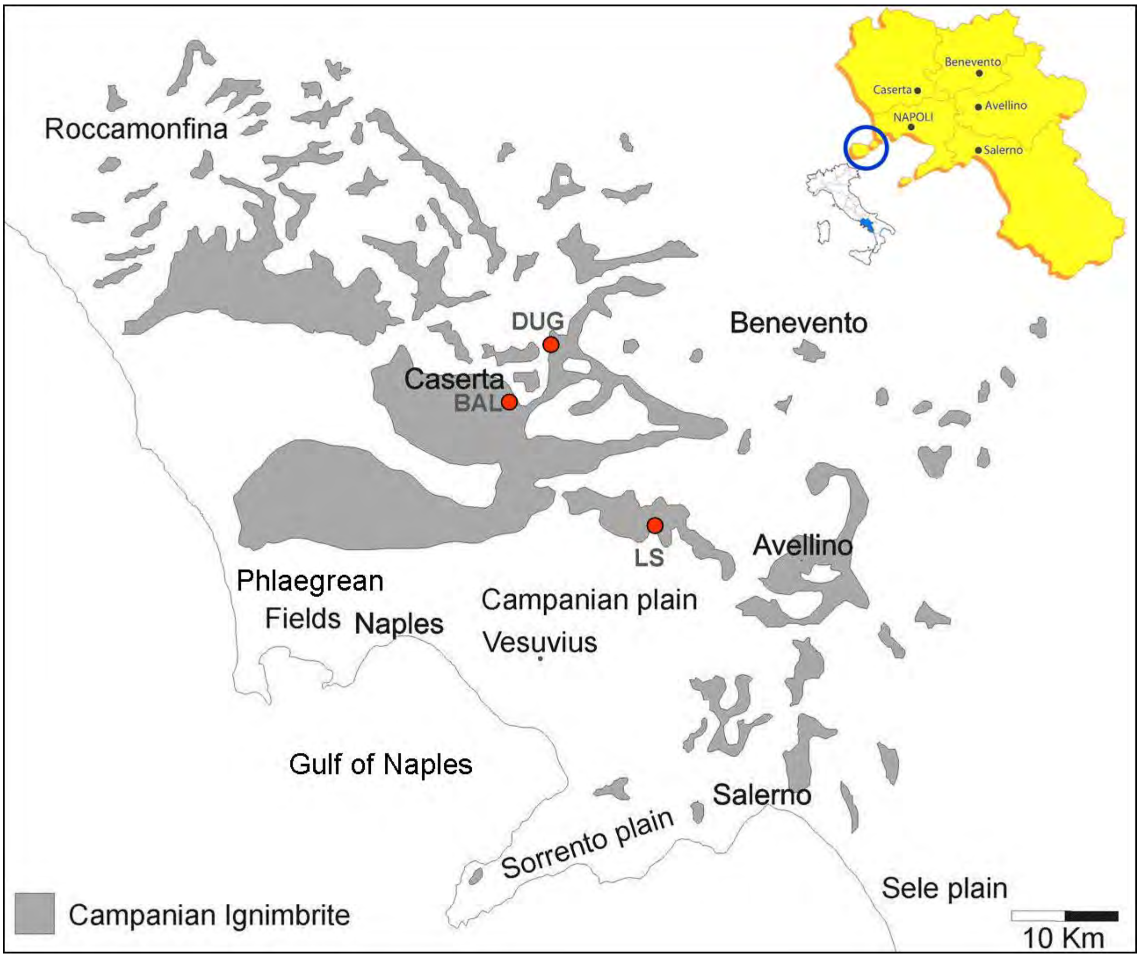

Figure 1 – Sketch map of Campanian Ignimbrite outcrops in Campanian Plain. The circle in the insert shows the location of the Ischia and Procida islands (from ref. 7, modified).
Legend: BAL = Balzarama; DUG = Dugenta; LS = La Schiava.

Geology

The Campanian Plain is characterized by a succession of ignimbritic deposits spanning up to about 270 ky b.p. in age (2). The most relevant deposit is represented by the Campanian Ignimbrite (39 ky) (2), the product of the main explosive activity in the Mediterranean region during the Quaternary Period (3). It is made up of a basal layered Plinian pumice fall deposit (PPF) overlain by a stratified, ashy to pumiceous or scoriaceous block ignimbrite. The overlying Campanian Ignimbrite is a pyroclastic current deposit outcropping mostly in the Campanian Plain (Fig. 1) and in the valleys of the Apennine chain up to 1000 m above sea level. The parental pyroclastic current covered an area >30,000 km^2. Based on internal structures (e.g. graded bedding), textures and components, four stratigraphic units were identified throughout the ignimbritic sequence. The lowermost unit is a stratified and incoherent ash to sandy deposit (Unconsolidated Stratified Ash Flow, USAF). Its thickness ranges from a few cm to 50 cm. A welded grey ash deposit (Welded Grey Ignimbrite, WGI), several meters thick, overlies the USAF unit. WGI is made up of black scoriae with subordinate lithics and crystals embedded in an ashy matrix. WGI is overlain by a Lithified Yellow Tuff (LYT) made up of an ashy matrix with rounded lapilli to dispersed block pumice clasts. The uppermost incoherent unit is made up of coarse pumice clasts within an ashy matrix (Coarse Pumice Flow, CPF).

Figure 2 – LS quarry (see Fig. 1), Comiziano, some 26 km, NE of Naples.

Volcanological and mineralogical evidence allows reconstruction of processes that affected the Campanian Ignimbrite after emplacement. A remarkable event during this eruption was the emplacement of the WGI unit formed by agglutination of particles settling from the base of a high-temperature parental flow. The temperature estimated for this distal *facies* was >600°C (4). The WGI unit, likely characterized by higher and more prolonged temperatures (5, 6), was affected by welding processes and authigenic feldspathization that, in some places (Faicchio, some 30 km NW of Benevento, see Fig. 1), led to the almost complete transformation (close to 90 wt%) of the precursor glassy fraction. On the basis of evidence in Castel S. Giorgio, Dugenta, and Balzarama (Fig. 1) it was possible to identify the relationships existing between units that, from top to bottom are: an incoherent cover almost totally constituted by fresh glass and pyrogenic minerals (feldspars, pyroxene, mica); an intermediate deeply zeolitized yellow portion; an invariably welded basal grey portion resting on a thin succession of incoherent layers. The thickness of the three upper units is quite variable, but never exceeds about 24 m. Wherever it was possible to carry out detailed sampling of the transitional areas between LYT and WGI (Balzarama and Dugenta, Fig. 1), a progressive decrease in zeolite content and a constant increase in feldspars in passing from the yellow to the grey facies was observed. Field features suggest that these products were emplaced progressively from a single sustained pyroclastic current. An increase of emplacement temperature after the early depositional phase of the eruption (USAF) originated a welded unit (WGI unit) sandwiched between incoherent units. The glassy fraction of the hot, upper unit was leached by water percolation that caused a progressive increase of pH of the solution. The resulting alkaline solution went gradually through the still hot sheet of the volcanics giving rise to its complete zeolitization and lithification (LYT unit). At this time, also the uppermost, less welded, part of the WGI unit was slightly zeolitized as a consequence of reduced water circulation that transformed the small amount of residual glass. Successively, the lithification processes proceeded towards the upper portion of the succession that still retained a temperature adequate for zeolitization. The progressive variation of physico-chemical conditions of the system, temperature, pH and activities in solution of the different atomic species, favoured the crystallization of prevailing phillipsite with minor chabazite in the lower portion of the LYT unit, and of prevailing chabazite with minor phillipsite in the upper part. A progressive decrease of temperature, especially in the upper part of the pyroclastic succession, stopped the zeolitization front so that the uppermost unit (CPF), not involved in this process, preserves all its original textural features (7).

Zeolite occurrence: Philllipsite- and Chabazite-rich tuff

Mineralogy: The zeolitized yellow *facies* of the CI (LYT) is characterized by the occurrence of phillipsite and chabazite as prevailing epigenetic phases along with rare analcime and more frequent smectite. The main pyrogenic phase is feldspar (sanidine) in amounts never exceeding 30 wt.% and biotite. The amorphous component ranges between a few units to some tens of percent (7,8). In the following table the mineral composition ranges (wt.%) on dry basis of tuff samples coming from three outcrops of the Campanian Ignimbrite formation are presented (see Fig. 1) (8).

MIneral	BAL	DUG	LS
Phillipsite	14-34	7-24	14-46
Chabazite	3-42	4-47	12-41
Analcime	1-10	1	0-3
Smectite	3-7	4-6	4-7
Feldspar	21-31	19-21	17-24
Biotite	1-2	1	1
Glass	9-49	20-45	14-24

BAL = Balzarana; DUG = Dugenta; LS = La Schiava (see Fig. 1).

Ignimbrite chemistry: The following table reports the mean chemical composition of CI in its gray and yellow *facies* (wt. %) (8)

Composition

Oxide	Gray *facies*	Yellow *facies*
SiO_2	60.44	54.80
TiO_2	0.46	0.47
Al_2O_3	18.47	16.12
Fe_2O_3	3.91	4.10
MnO	0.18	0.16
MgO	0.68	0.82
CaO	2.32	3.95
Na_2O	4.54	1.09
K_2O	7.20	6.65
P_2O_5	0.11	0.09
LOI	1.75	11.83
Total	100.06	100.08

Cation exchange capacity The cation exchange capacity of the CI (whole rock), estimated according to Cerri et al. (9), ranges from 1.90 to 2.10 meq g^{-1}.

Zeolite chemistry **T**he mean chemical composition of the zeolites (phi = phillipsite; cha = chabazite) contained in the CI, estimated by EDS (water content by difference) are reported in the following table (wt. %) (8)

Oxide	BAL phi	BAL cha	DUG cha	LS phi	LS cha
SiO_2	54.14	52.89	53.50	55.14	52.37
TiO_2	0.11	0.08	0.11	0.09	0.05
Al_2O_3	18.01	17.62	17.01	18.07	16.76
Fe_2O_3	0.16	0.17	0.18	0.15	0.15
MnO	0.04	0.02	0.01	0.03	0.01
MgO	0.15	0.72	0.48	0.11	0.26
CaO	3.26	5.71	5.99	3.98	6.46
Na_2O	1.63	0.56	0.68	1.29	0.41
K_2O	7.73	4.46	3.40	7.32	3.98
Total	85.24	82.23	81.36	86.18	80.45

Chemical formulae (LS)

CI Phillipsite $|(Na_{0.52}K_{1.95})(Ca_{0.89}Mg_{0.03})|\ [Al_{4.46}Si_{11.54}O_{32}]\ 9.65\ H_2O$

CI Chabazite $|(Na_{0.13}K_{0.84})(Ca_{1.15}Mg_{0.06})|\ [Al_{3.27}Si_{8.68}O_{24}]\ 10.80\ H_2O$

Physical and mechanical properties: The petro-physical data of CI (whole units), averaging the results of numerous tests, performed over the years (10) are summarized In the following table. Data have been obtained with the standard procedures *NorMaL UNI EN: No. 1925, 2000; No. 13755, 2002; No. 1926, 2004; No. 14581, 2005; No. 14579, 2005).**

Parameter	Range	Mean value
Dry density (kN m^{-3})	9.85-12.10	10.97
Specific gravity (kN m^{-3})	21.51-23.13	22.68
Compactness degree	-	0.48
Capillary absorption (gr $cm^{-2}\cdot s^{1/2}$)	0.012-0.015	0.014
Absorption coefficient (%)	28.49-40.43	34.73
Open porosity (%)	46.85-57.20	51.61
Average pore radius (μm)	0.56-0.79	0.66
Specific surface area (m^2 g^{-1})	8.07-9.60	8.91
Total pore volume (cm^3 g^{-1})	0.33-0.41	0.36
Uniaxial compressive strength (MPa)	4.11-8.02	6.45
Linear thermal expansion coeff. (10^{-6}mm/mm°C^{-1})	[-28.50]-[-12.00]	-18.07
Volumetric strain (%)	0.3-1.01	0.49
Dry ultrasonic speed (m/s)	1672-2204	1777
Saturated ultrasonic speed (m/s)	1536-2092	1621

* NorMaL and UNI EN are acronyms for standard procedures developed by CNR (National Research Council) and Italian Standards Agency, respectively.

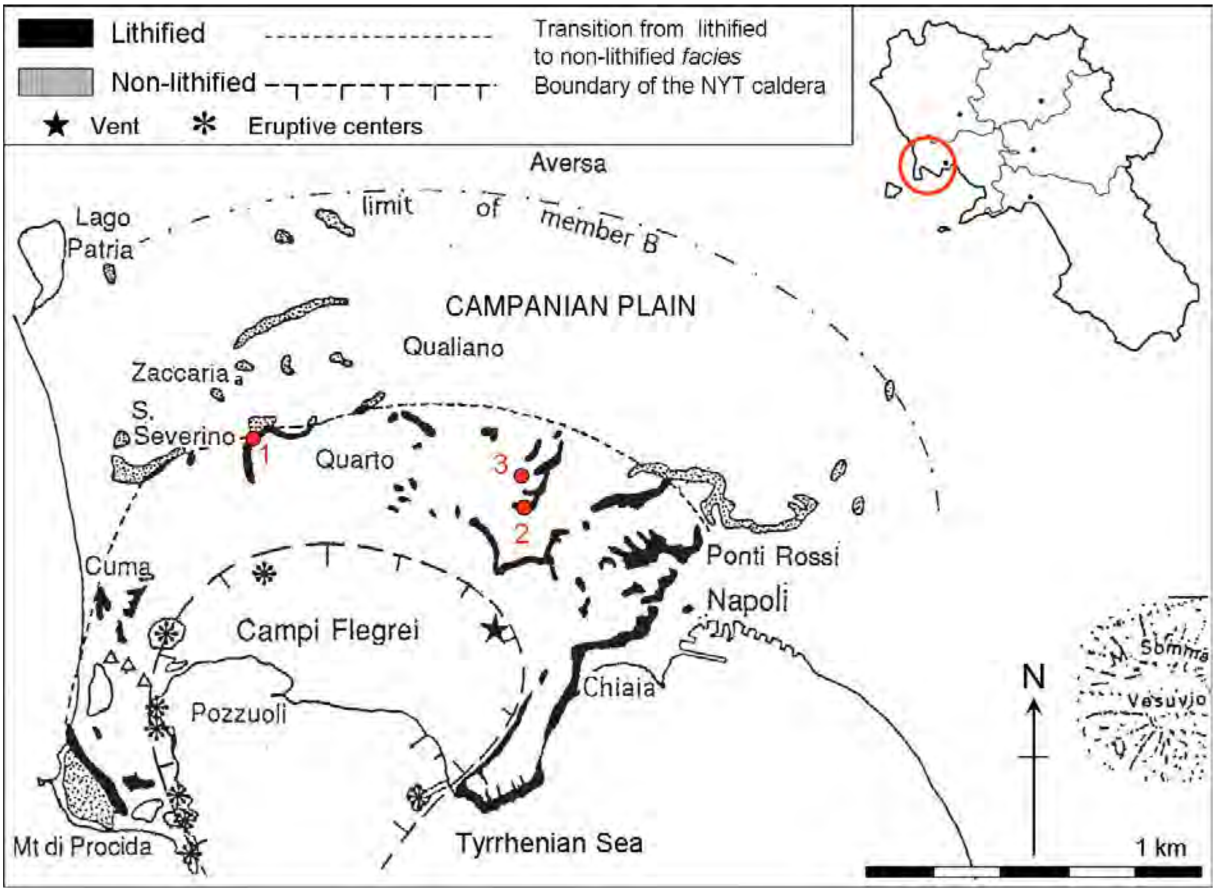

Figure 3 – Sketch map of Neapolitan yellow tuff outcrops in Campi Flegrei (from Fig. 1, ref. 12, modified).
Legend: 1 = Liccarblock (LB); 2 = Edificante (EDI); 3 = Zara (ZA).

Geology

The NYT occurs as thick and widespread pyroclastic deposits on the periphery of Campi Flegrei, within the city of Napoli and in the Campanian Plain (Fig. 3). The inferred source for the NYT is located in the northeastern part of Campi Flegrei and the tuff crops out at a maximum distance of 31 km from this vent. Two different Members (A and B from bottom to top) have been recognized on the basis of field characteristics and granulometric parameters. Member A is made up of at least six fall units, interbedded with numerous ash layers. Member B is found up at a distance of 14 km from the vent. In general, it can be distinguished from Member A by its coarser grain size and by the presence of thicker massive units. de' Gennaro et al. (11) suggested that zeolitization in NYT took place soon after eruption in a well-insulated thermal system in the presence of hot aqueous solutions of hydromagmatic origin, whose ionic composition was controlled by equilibrium glass hydrolysis. The presence of wet facies accounts for the presence of sufficient water necessary for the triggering of secondary minerogenetic processes. The vertical and lateral variations in lithification grade reflect the effects of two factors: fluctuating emplacement conditions and thermal dispersion. The vertically variable zeolite content within Member B is related to a change in physical conditions (water content, temperature) during emplacement of the Member. The reduction in lithification grade towards the base and top of the sequence suggests that the heat loss towards the atmosphere and substrate affected the zeolitization process, probably cooling the outer part of the deposit too quickly for zeolitization. The lack of authigenic feldspars is a further indication that the minerogenetic process was interrupted, limiting any further mineral evolution towards more stable phases.

Figure 4 – NYT quarry in Quarto (see Fig. 3). **a**: pozzolan (unlithified original volcaniclastic material); **b**: Neapolitan yellow tuff.

Zeolite occurrence: Phillipsite- and Chabazite-rich tuff

Mineralogy: NYT is characterized by the presence of phillipsite and chabazite as prevailing epigenetic phases along with analcime and smectite. Feldspar (sanidine) is the most abundant pyrogenic phase (30 wt.%). Amorphous phases range between a few units to some tens percent. In the following table the percent composition ranges (wt.%) on dry basis of tuff samples coming from three quarries (see Fig. 3) are presented (13).

MIneral	EDI	ZA	LB
Phillipsite	48	48-60	34
Chabazite	4	3-10	13
Analcime	3	5-11	8
Smectite	13	6-8	6
Feldspar	20	24-26	28
Biotite	1	>1	>1
Glass	11	5-13	10

EDI = Edficante; ZA = Zara; LB = Liccarblock (see Fig. 3).

Tuff chemistry: The following table reports the wt.% chemical composition of some NYT samples (14).

Sample	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	SrO	BaO	Na_2O	K_2O	LOI	Total
NP	52.08	16.52	3.50	1,.2	2.71	0.01	0.05	2.06	8,67	13.72	100.34
PI	52.16	18.40	3.65	1,.3	2.13	0.01	0.08	2,52	7.47	12.30	100.25
MB	53.02	17.55	3.60	1,.3	3.14	-	0.04	2,83	6.81	12.20	100.42
TG	51.52	18.45	4.02	0.82	2.28	0.02	0.07	3,18	7.71	12.30	100.37
GS	54.06	16.00	2.75	0.72	1.43	0.02	0.06	3,99	7.83	13.30	100.16
LI	51.60	17.59	2.05	1.29	3.42	0.04	0.09	3,33	7.23	13.50	100.14

Legend Quarries and outcrops in Campi Flegrei: NP: Nuovo Policlinico; PI: Pianura; MB: Monte Barbaro; TG: Torregaveta; GS: Grotta del Sole; LI: Licola

Cation exchange capacity

The cation exchange capacity of the NYT (whole rock), estimated according to Cerri et al. (9), ranges from 2.00 to 2.20 meq g^{-1}.

Zeolite chemistry

The mean chemical composition of the zeolites contained in the NYT, estimated by EDS (water content by TG analysis), are reported in the following table (wt. %) (15)

Oxide	Phillipsite	Chabazite
SiO_2	55.17	52.73
Al_2O_3	17.61	16.77
Fe_2O_3	0.26	0.17
MgO	0.13	0.35
CaO	1.99	4.53
Na_2O	2.99	1.78
K_2O	9.22	5.28
H_2O	12.65	18.39

Chemical formulae

NYT phillipsite $|(Na_{1..21}K_{2.42})(Ca_{0.45}Mg_{0.04})|\ [Al_{4.35}Si_{11.57}O_{32}]\ 8.83\ H_2O$

NYT chabazite $|(Na_{0.57}K_{1.11})(Ca_{0.80}Mg_{0.10})|\ [Al_{3.25}Si_{8.68}O_{24}]\ 10.10\ H_2O$

Crystallography

The unit cell parameters of phillipsite from Grotta del Sole (see the table reporting Tuff chemistry) are as follows (16):

a [Å]	b [Å]	c [Å]	β [°]	Space group
9.9792(5)	14.2075(8)	8.7071(8)	124.978(6).	P21/m

Physical and mechanical properties:

The petro-physical data of NYT (whole units), averaging the results of numerous tests, performed over the years (17) are summarized In the following table. Data have been obtained with the standard procedures *NorMaL UNI EN: No. 1925, 2000; No. 13755, 2002; No. 1926, 2004; No. 14581, 2005; No. 14579, 2005).**

Parameter	Range	Mean value
Dry density (kN m^{-3})	8.75-12.04	10.93
Specific gravity (kN m^{-3})	21.59-24.17	22.75
Compactness degree	-	0.48
Capillary absorption (gr $cm^{-2}\cdot s^{1/2}$)	0.019-0.036	0.030
Absorption coefficient (%)	30.01-46.29	37.06
Open porosity (%)	39.50-63.28	51.81
Average pore radius (μm)	0.03-16.08	5.27
Specific surface area (m^2 g^{-1})	13.02-21.54	16.93
Total pore volume (cm^3 g^{-1})	0.27-0.45	0.35
Uniaxial compressive strength (MPa)	0.70-11.90	5.59
Linear thermal expansion coeff. (10^{-6}mm/mm°C^{-1})	[-35.50]-[-24.19]	-24.19
Volumetric strain (%)	0.23-1.15	0.54
Dry ultrasonic speed (m/s)	1462-2397	1847
Saturated ultrasonic speed (m/s)	1382-2233	1720

* NorMaL and UNI EN are acronyms for standard procedures developed by CNR (National Research Council) and Italian Standards Agency, respectively.

Reserves and production: The total estimated zeolite reserves in megatons (Mt) in the three volcanic districts of the Campania region are reported In the following table (18). The whole annual production capacity is roughly 950.000 tons.

District	CI, Mt	NYT, Mt
Benevento	41	
Caserta	427	
Napoli	10	9.5

Main applications: The possibility to use Campanian tuffs in different technological fields such as municipal and industrial wastewaters treatments, active additions in pozzolanic cements, lightweight aggregates production for structural cement, constituent of three-component (N, P, K) mineral fertilizers, has been demonstrated. The present main fields of use of CI and NYT are:

(a) Agriculture
soil additive**;**
component of feeding mixtures for animals**;**
litter additive**.**

(b) Construction
Some 80% of tuff production is being exploited for manufacturing dimension stone for the building industry (see Fig. 2).

References

1. http://www.ov.ingv.it/italiano/flegrei/storia/storia.htm.
2. De Vivo B, Rolandi G, Gans PB, Calvert A, Bohrson WA, Spera FJ, Belkin HE (2001) New constraints on the pyroclastic eruptive history of the Campanian volcanic Plain (Italy). Mineral Petrol 73: 47–65.
3. Barberi F, Innocenti F, Lirer L, Munno R, Pescatore T, Santacroce R (1978) The Campanian Ignimbrite: a major prehistoric eruption in the Neapolitan area (Italy). Bull Volcanol 41(1): 1–22
4. Di Girolamo P, Downey WS, Incoronato A, Nardi G (1984) First data on emplacement temperatures of the Campanian Ignimbrite (Southern Italy). Department of Earth Sciences, Federico II University, Napoli (unpublished report).
5. Riehle JR, Miller TF, Bailey RA (1995) Cooling, degassing and compaction of rhyolitic ash flow tuffs: a computational model. Bull Volcanol 57: 319–336
6. Hall A (1998) Zeolitization of volcaniclastic sediments: the role of temperature and pH. J Sedim Res 68(5): 739–745
7. Cappelletti P, Cerri G, Colella A, de' Gennaro M, Langella A, Perrotta A, Scarpati C (2003): Post-eruptive processes in the Campanian Ignimbrite. Mineral Petrol, 79, 79-97.
8. Langella A, Bish DL, Cappelletti P, Cerri G, Colella A, de Gennaro R, Graziano SF, Perrotta A, Scarpati C, de' Gennaro M (2013) New insights into the mineralogical facies distribution of Campanian Ignimbrite, a relevant Italian industrial material. Applied Clay Science 72, 55–73.
9 Cerri G, Langella A, Pansini M, Cappelletti P (2002) Methods for the determination of cation exchange capacities for clinoptilolite-rich rocks of the Logudoro region in northern Sardinia, Italy. Clays Clay Min, 50, 127-135.
10 Langella A, Bish DL, Calcaterra D, Cappelletti P, Cerri G, Colella A, Graziano SF, Papa L, Perrotta A, Scarpati C, de' Gennaro M (2013) L'Ignimbrite Campana (IC), In de' Gennaro M, Calcaterra D, Langella A (Eds), Le Pietre Storiche della Campania dall'oblio alla riscoperta, Luciano Editore, Napoli, 2013, p. 155-177.
11. de' Gennaro M, Cappelletti P, Langella A, Perrotta A, Scarpati C (2000) Genesis of zeolites in the Neapolitan Yellow Tuff: geological, volcanological and mineralogical evidence. Contrib Mineral Petrol 139, 17-35.
12. Scarpati C, Cole P, Perrotta A (1993) The Neapolitan Yellow Tuff – A large volume multiphase eruption from Campi Flegrei, southern Italy. Bull Volcanol 55: 343-356.
13. Lab of Applied Mineralogy, Department of Earth Sciences, Federico II University, Napoli (unpublished reports).
14. de' Gennaro M, Franco E, Langella A, Mirra P, Morra V (1982) Le phillipsiti dei tufi gialli del Napoletano. Period Mineral 51, 287-310.
15. Lab of Applied Mineralogy, Department of Earth Sciences, Federico II University, Napoli (unpublished data).
16. Gatta GD, Cappelletti P, Langella A (2010) Eur J Mineral 22, 779–786.
17. Colella A, Calcaterra D, Cappelletti P, Di Benedetto C, Langella A, Papa L, Perrotta A, Scarpati C, de' Gennaro M (2013) Il Tufo Giallo Napoletano, In de' Gennaro M, Calcaterra D, Langella A (Eds.), Le Pietre Storiche della Campania dall'oblio alla riscoperta, Luciano Editore, Napoli, 2013, p. 129-155.
18. Giunta Regionale della Campania – Piano regionale delle Attività Estrattive – Relazione illustrativa generale, 2003.

Further information on exploited and unexploited deposits is available from Professor Maurizio de Gennaro, contactable by email at: maurizio.degennaro@unina.it.