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Volcanological and geochemical features of young pyroclastic levels (< 12 ka) in the urban area of Naples (S. Italy)

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ABSTRACT. — Two stratigraphic sections (Palazzo Reale and Castel Nuovo), found in Naples during archaeological excavations, were investigated from the geochemical and volcanological points of view. These sections consist of Phlegrean and Vesuvian pyroclastic rocks, emitted after the emplacement of the Neapolitan Yellow Tuff (NYT; 12 ka).

Pyroclastic products belonging to Pomici Principali (trachyphonolitic), Soccavo 4 (trachytic) and Minopoli 2 (shoshonitic) levels were identified in the Palazzo Reale section. These eruptions belong to the first epoch of post-NYT magmatic activity. The Pomici Principali deposit, more than 2 m thick, shows no appreciable change in chemical composition upwards, due to the tapping of a chemically homogeneous magma chamber. The other two pyroclastic layers reach a total thickness of about 30 cm.

Trachytic rocks with higher contents of incompatible elements (Nb 52-67 ppm, Zr 374-500 ppm), correlated to the last epoch of the Phlegrean magmatic activity (4.8-3.8 ka BP), are found in the Castel Nuovo section. The correlation between trachytic rocks at Castel Nuovo and the last-epoch products of the Phlegrean magmatic activity is confirmed by the lack of the Pomici Principali deposit and by their chemical affinity; these rocks generally display contents of incompatible elements higher than the products of the first and second post-NYT epochs. This is related to the long quiescence period between the two last phases of magmatic activity (about 3.5 ka), during which the Phlegrean magmatic system mainly evolved by fractional crystallization processes.

RIASSUNTO. — Sono state studiate due sezioni stratigrafiche, portate alla luce durante scavi archeologici effettuati nel centro di Napoli, di formazioni piroclastiche flegree successive all'eruzione del Tufo Giallo Napoletano (TGN) ed un deposito di origine vesuviana.

Nella sezione di Palazzo Reale sono stati riconosciuti i prodotti piroclastici delle seguenti eruzioni: Pomici Principali (di composizione trachifonolitica), Soccavo 4 (di composizione trachitica) e Minopoli 2 (di composizione shoshonitica). Tali eruzioni appartengono alla prima epoca dell'attività magmatica post-TGN. Il deposito delle Pomici Principali, avente uno spessore superiore a 2 metri, non esibisce significative variazioni geochimiche; ciò è da mettere in relazione allo svuotamento di una camera magmatica sostanzialmente non zonata. Gli altri due livelli piroclastici raggiungono uno spessore totale di circa 30 cm.

Nella sezione di Castel Nuovo sono stati rinvenuti prodotti trachitici aventi un maggior contenuto in elementi incompatibili (Nb = 52-67 ppm e Zr = 374-500 ppm). Tali depositi piroclastici sono stati

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correlati all'ultima epoca dell'attività magmatica flegrea (4.800-3.800 anni fa). Questa correlazione si basa sia sulla mancanza del deposito delle Pomici Principali (che, per la loro ampia diffusione, costituiscono un ottimo marker stratigrafico), sia sulla similitudine geochimica con i prodotti di quest'ultima epoca, i quali mostrano, in generale, un maggiore contenuto in elementi incompatibili rispetto alle prime fasi di attività magmatica successive all'eruzione del TGN. L'elevato contenuto di elementi incompatibili nei magmi eruttati è verosimilmente collegato al lungo periodo di quiescenza che ha separato le due ultime fasi di attività vulcanica (circa 3.500 anni), durante il quale il sistema magmatico flegreo si è evoluto principalmente via cristallizzazione frazionata.

KEY WORDS: *Campi Flegrei (Phlegraean Fields), volcanology, geochemistry, trachyte, trachyphonolite, Napoli (Naples)*

INTRODUCTION

The present work deals with the geochemical and volcanological features of two stratigraphic sequences cut by archaeological excavations in the city of Naples (fig. 1), and allows better reconstruction of the recent volcanic and magmatic history of an area which is densely inhabited and therefore characterized by high volcanic hazard.

The city of Naples lies between the Campi Flegrei volcanic district to the west and the Somma-Vesuvius volcanic complex to the east (fig. 1). The volcanic products of these two districts cover a large part of the Campanian region, and are also recorded in the eastern Mediterranean area (e.g., layer Y5 of Keller *et al.*, 1978). The volcanic rocks outcropping in the Naples area mostly refer to the activity of the Campi Flegrei and, in particular, to the last 12 ka of their activity. Older lava flows, lava domes and pyroclastic rocks from tuff cones are found in the south-western part of the city (Cole *et al.*, 1994). The extensive urbanization of the city greatly hinders reconstruction of the stratigraphic sequence in the metropolitan area. In this context, newly exposed sections may be important for better knowledge of the stratigraphy and the magmatic processes which occurred in a such complex volcanic district.

VOLCANOLOGICAL AND PETROLOGICAL BACKGROUND

The Campi Flegrei cover an active volcanic area characterized by a large calderic depression, alternatively related either to the eruptions of the Campanian Ignimbrite (CI; ~ 37 ka BP; Rosi *et al.*, 1983; Rosi and Sbrana, 1987) or the Neapolitan Yellow Tuff (NYT; ~ 12 ka BP; Di Girolamo *et al.*, 1984; Scarpati *et al.*, 1993). Instead, Orsi *et al.* (1996) interpreted the Phlegrean depression as a nested caldera structure related to both eruptions. The collapse related to the NYT is included in the larger CI caldera. The Phlegrean volcanic products are dominantly pyroclastic, with only rare lava flows and domes. Felsic rocks (trachyte and trachyphonolite) predominate over basic and intermediate ones (latite and shoshonitic basalt; Di Girolamo *et al.*, 1984; Pappalardo *et al.*, 2002). All the juvenile products belong to shoshonitic rock series.

Many authors have studied the evolution over the last 12 ka of the Campi Flegrei magmatic system. Armienti *et al.* (1983) interpreted the evolution from trachybasalt to trachyte/phonolite by fractional crystallization in a large, essentially unitary, magma chamber. Beccaluva *et al.* (1990) suggested the presence of distinct mafic parental melts fractionating independently towards more felsic types within a complex feeding system. Selective contamination of magma, located in the deeper part of the magma chamber, by K- and Sr-rich volatiles derived from heated wall rocks, has also been hypothesized (Villemant, 1988; Civetta *et al.*, 1991). Recently, D'Antonio *et al.* (1999), on the basis of new chemical and isotopic data on volcanic rocks younger than the NYT, recognized three distinct magmatic components characterized by distinct Sr-isotope ratios which evolved in a complex

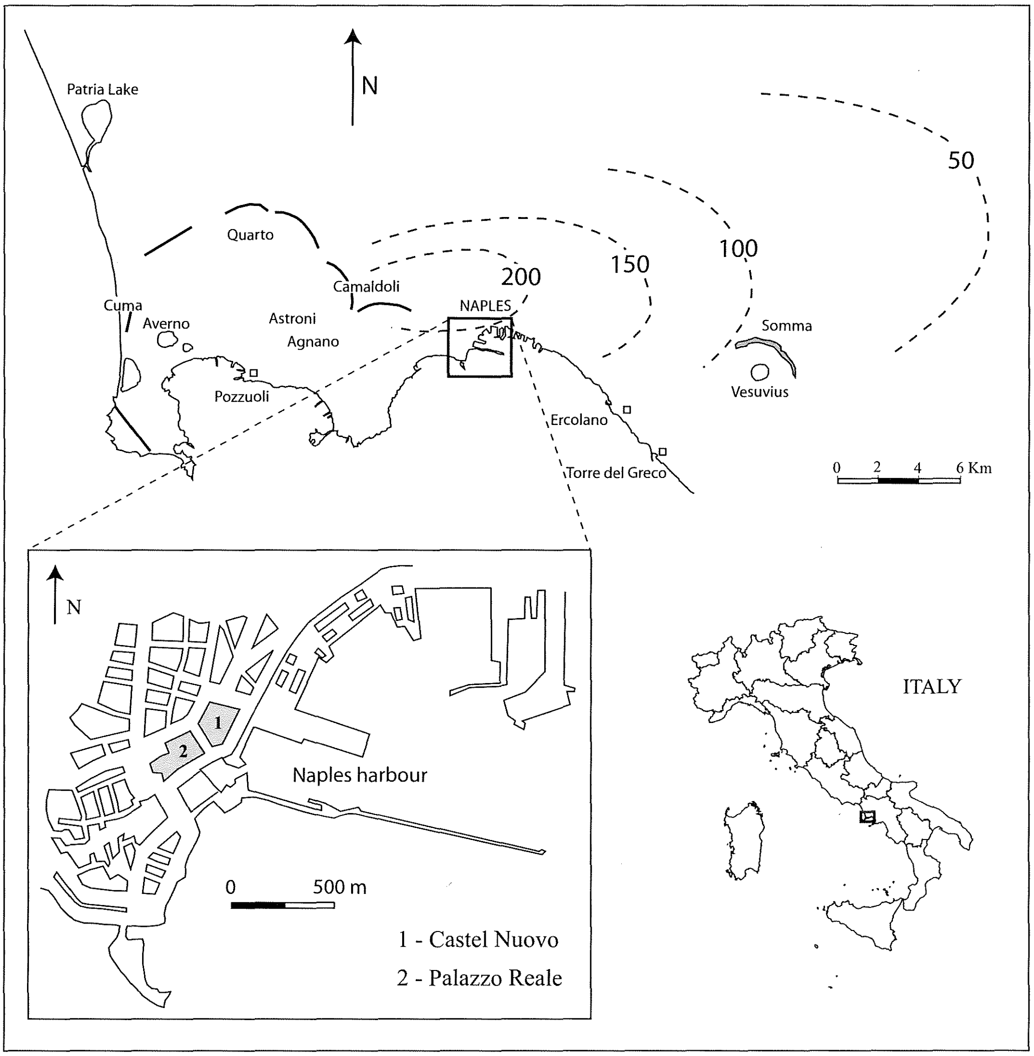

Fig. 1 – Location map of study area and distribution of Pomici Principali (isopachs in cm; according to Rosi and Sbrana, 1987).

system; fractional crystallization and mixing between different batches of magma were also proposed for the evolution of the post-NYT Phlegrean magmatic system. Recently, Di Vito *et al.* (1999) divided the volcanic activity of the last 12 ka (post-NYT emplacement) into three epochs (respectively 12-9, 8.6-8.2 and 4.8-3.8 ka BP), with more than 70 eruptions, some of which covered the western part of the urban area of Naples (i.a., Pomici Principali, Agnano-Monte Spina). The volcanic activity of the last 12 ka was confined inside the NYT caldera or along its margin. Moreover, in the second and third epochs, activity mainly took place in the north-eastern part of the Campi Flegrei (Di Girolamo *et al.*, 1984; Orsi *et al.*, 1996; Di Vito *et al.*, 1999). The present activity of the Campi Flegrei is characterized by post-volcanic phenomena (fumarole and hydrothermal activity) in the Bacoli-Lucrino, Solfatara, Agnano, and Ischia areas.

STUDY SECTIONS

During archaeological excavations in the Palazzo Reale and the Castel Nuovo of Naples (fig. 1), some sequences of pyroclastic deposits were exposed. The stratigraphic section below Palazzo Reale is not continuous. Three pyroclastic sequences (named levels 1, 2 and 3) were found in two halls of the palace and in a sort of chamber connected with one of these halls through a well; the reconstructed section is shown in fig. 2.

Level 1 is exposed in the chamber, and consists of a fallout sequence of alternating pumice and ash beds, with a total thickness of about 230 cm. These characteristics clearly show that the deposit belongs to the Pomici Principali eruption (10.32±0.05 ka; Di Vito *et al.*, 1999), the largest subaerial eruption of Campi Flegrei in last 12 ka (0.14 km^3 DRE – Dense Rock Equivalent; Lirer *et al.*, 1987). The Pomici Principali tephra cover an area of about 350 km^2 and mainly consists of alternating pumice beds and ash fallout layers, the number of which increases approaching the vent (Rosi and Sbrana, 1987). Di Vito *et al.* (1999) subdivided the Pomici Principali unit, from the base upwards, into three members, named A (massive, fine ash layer), B (alternating coarse pumice and ash beds) and C (fine ash, sandwave surge beds). The isopachs of the fallout deposits are generally elongated E-NE (fig. 1) and the total thickness of the layers ranges from 3 m near the source area to 10-15 cm at about 40 km from the vent (Lirer *et al.*, 1987). The eruption vent was located in the Agnano area (Rittmann, 1950; Scherillo and Franco, 1960; Di Girolamo *et al.*, 1984; Rosi and Sbrana, 1987); new stratigraphic and volcanological data carried out by Di Vito *et al.* (1999) moved the inferred vent source to the Astroni area.

The investigated deposit in the excavation is made up of seven generally well sorted pumice beds containing scattered lithic fragments, interstratified with thin ash layers. Following the nomenclature proposed by previous authors (Di Girolamo *et al.*, 1984, and references therein) we named the pumice layers α, β1-β2-β3 (3β), β, γ, δ.

Layer α (40 cm thick) shows a weak reverse and direct grading at base and top, respectively. The pumice is dark grey in colour and has a maximum diameter of about 4 cm. Lithics are rare and millimetric. In layer β1 (20 cm thick), the pumice has a diameter up to 3 cm and is reverse graded. Layers β1, β2 and β3 constitute level 3β (40 cm thick), in which lithic fragments are diffuse and have a maximum diameter of 2 cm. β is the thickest layer (70 cm), with reverse grading in the first 10 cm and dark scoriae, up to 7 cm in diameter, at the top. The pumice becomes pink upwards. This feature is also found in upper layer γ (30 cm thick) with many lithic fragments. The last pumice bed, δ (15 cm thick), is directly graded with diffuse lithic fragments.

The ash beds separating the pumice layers are only a few cm thick, generally less than 10 cm. They are massive layers containing scattered small pumice and lithic fragments and, sometimes, accretionary lapilli. Lithic fragments in the various pyroclastic layers are represented by fresh and hydrothermalized lavas.

Level 1 breaks off at the bottom of the well dug in the hall, where level 2 outcrops. This deposit is composed of a 10 cm-thick bed of small pumice with cineritic matrix and, in the other hall, is covered by level 3. The latter pyroclastic deposit is composed of alternating ashy and pumice beds, with a total thickness of about 20 cm.

The section beneath Castel Nuovo (about 200 metres west of Palazzo Reale) consists of pyroclastic fallout and surge deposits from at least seven eruptive events, separated from each other by paleosoils or humified zones. The layers are named A to G, from base to top (fig. 2). At the bottom is a 25 cm-thick brown paleosoil covered by a fallout deposit (30 cm thick; layer A), composed of ash with scattered

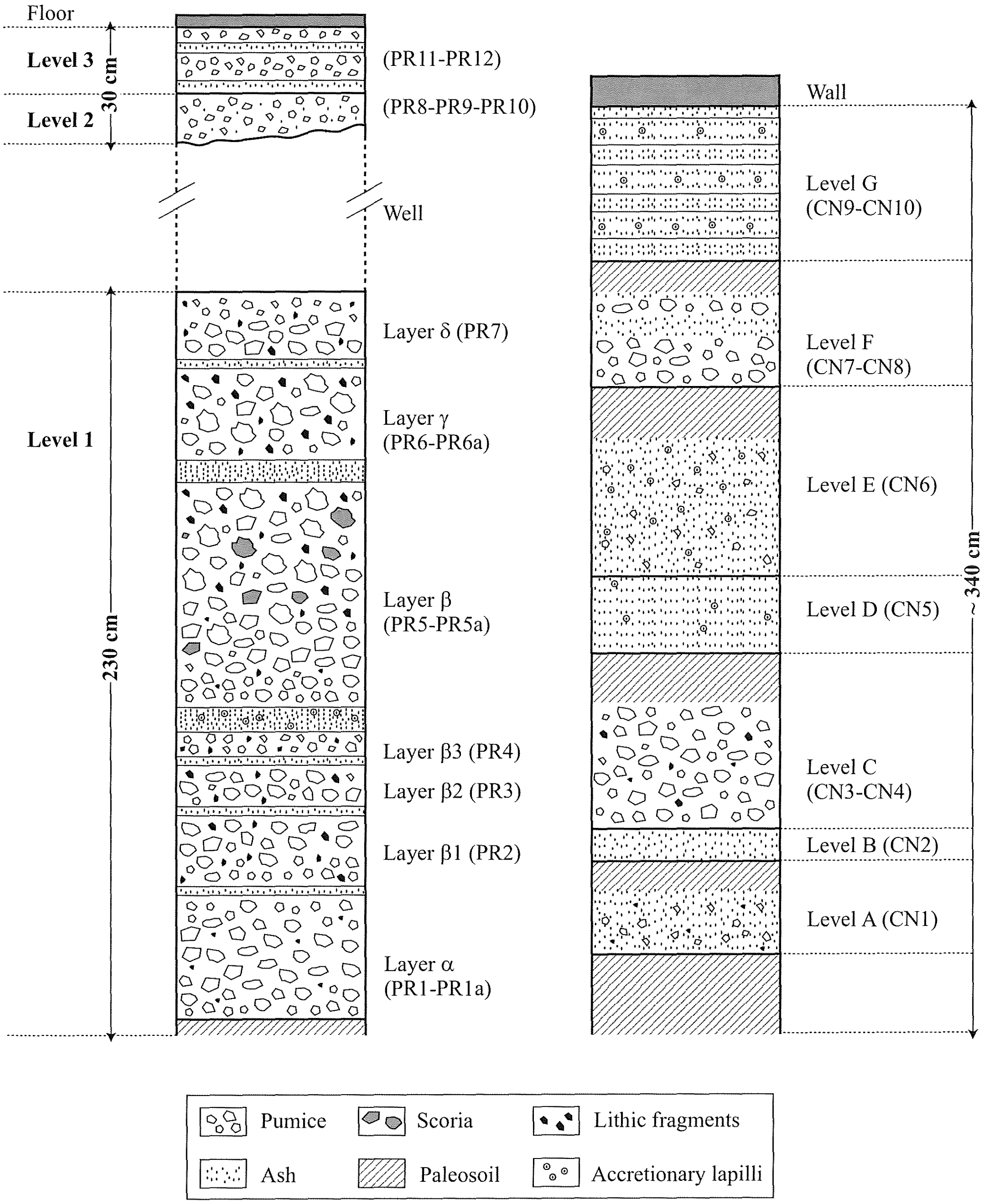

Fig. 2 –Stratigraphic sections of Palazzo Reale (left) and Castel Nuovo (right). Locations are shown in Fig. 1.

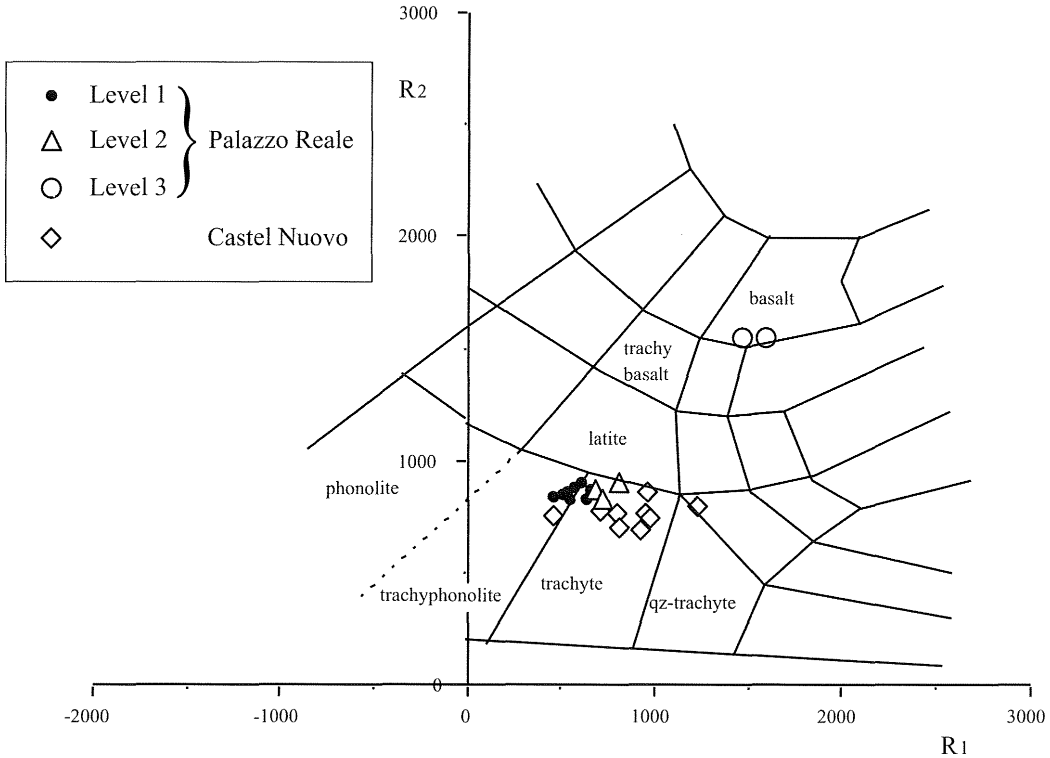

Fig. 3 – R1R2 diagram (R1 = 4Si – 11(Na + K) – 2(Fe + Ti), R2 = 6Ca + 2Mg + Al; De La Roche *et al.*, 1980) of juvenile products from Palazzo Reale and Castel Nuovo.

elements: SiO_2 (57.29-58.36 wt%), MgO (1.67-2.01 wt%), P_2O_5 (0.13-0.20 wt%), K_2O (8.11-8.87 wt%) do not show significant variations; the K_2O/Na_2O ratio is always higher than 2. Incompatible element contents of Nb and Zr are roughly constant (38-41 and 275-286 ppm, respectively); Ba, Sr and Rb also show restricted variations (1673-1714, 842-872 and 288-310 ppm, respectively). All the data indicate a homogeneous composition for the Pomici Principali tephra.

The pumice belonging to level 2 (samples PR8 to PR10) is a trachyte with a chemical character very similar to that of the Pomici Principali. SiO_2, MgO and P_2O_5 are about 58.0, 1.8 and 0.24 wt%, respectively. K_2O is around 8.1 wt% and the K_2O/Na_2O ratio is higher than 2. Nb and Zr contents are within the range shown by the Pomici Principali juvenile fragments, while Ba and Sr values are lower (about 1470 and 800 ppm, respectively).

The upper level of this section (samples PR11 and PR12; level 3) has a shoshonitic composition, with higher contents of MgO and CaO (about 5.5 and 9.0 wt% respectively), Sc (~30 ppm), and V (~200 ppm) and lower Zr (184-188 ppm), Nb (21-23 ppm) and Rb (~200 ppm) than the trachyphonolite and trachyte of levels 1 and 2; on the other hand, Ba (1788-1835 ppm), Sr (864-881 ppm) and LREE are similar.

The pyroclastic products of the stratigraphic section of Castel Nuovo are mainly made up of trachyte. The uppermost level (G) has a different composition and will be discussed separately. Some samples are qz-normative

(0.6-3.7%), probably due to alteration (as also indicated also by high LOI values). SiO_2 is around 60 wt%; MgO is low and rarely reaches values higher than 1 wt%; K_2O ranges from 7.8 to 8.7 wt%, with K_2O/Na_2O ratios always higher than 2. The contents of immobile, incompatible elements are higher than in the samples of the Palazzo Reale section: Zr and Nb range respectively between 374 and 500 ppm and between 52 and 67 ppm. Two samples of the major coarse deposits (levels C and F), located at the bottom and top of the layer, were analysed. Only level C (samples CN3 and CN4) shows an appreciable upward change in trace element contents.

The samples from the upper level of the Castel Nuovo sequence (CN9 and CN10) are strongly altered and have high LOI; CaO values are higher than those expected for evolved trachyte. X-Ray diffraction patterns show the presence of calcite and analcime as prevailing phases, plus feldspars, clinopyroxene, kaolinite and quartz.

Discussion

The possibility of studying buried volcanic sequences exposed during archaeological excavations is important for better knowledge of geological and volcanological evolution in highly urbanized areas with active volcanic activity.

Level 1 of the Palazzo Reale section displays the volcanological characters of the Pomici Principali tephra. The total thickness is about 230 cm; this value is consistent with the hypothesized isopachs reconstructed by various authors (Lirer *et al.*, 1987; Rosi and Sbrana, 1987). From a geochemical point of view, the pumice samples of this eruption have a uniform, trachyphonolitic composition without any systematic compositional variation with stratigraphic height, in agreement with other Pomici Principali deposits studied in different outcrops (Lirer *et al.*, 1987; D'Antonio *et al.*, 1999).

Selected trace element concentrations of the studied samples together with some data from the literature on post-NYT Phlegrean eruptions (Lirer *et al.*, 1987; Ghiara *et al.*, 1989-1990; D'Antonio *et al.*, 1999; De Vita *et al.*, 1999), are plotted in variation diagrams (fig. 4).

The Pomici Principali samples plot within the narrow field of the literature data, confirming the general uniform composition of the juvenile products of this eruption

Rosi and Sbrana (1987) found very subordinate juvenile products with latitic composition at the top of a sequence of Pomici Principali, and suggested a geochemically zoned magma chamber for this eruption. However, trachyphonolitic products represent almost the whole deposit, and their chemical composition does not show any important variations in major or trace elements, like those of other Campi Flegrei eruptions related to the tapping of a zoned magma chamber (Di Girolamo, 1970; Melluso *et al.*, 1995; Civetta *et al.*, 1997; De Vita *et al.*, 1999). This may mean that the eruption was triggered when a latitic magma reached a chamber filled with more highly evolved magma. The homogeneous trachyphonolitic composition suggests that this magma, once it had reached the upper crustal zone, stopped for a time short enough not to differentiate later.

In the last 12 ka, mafic rocks have only been emitted from the Minopoli and Pigna San Nicola volcanoes (D'Antonio *et al.*, 1999). Fig. 4 plots the level 3 shoshonite in the field of the products of Minopoli, which have the lowest contents in the most incompatible elements (Zr, Nb) of the Phlegrean products of the last 12 ka. Two eruptions are recorded from this vent: Minopoli 1 and Minopoli 2, pre- and post-Pomici Principali eruptions, respectively (Di Vito *et al.*, 1999). Therefore, sedimentological, stratigraphic and geochemical characteristics indicate that level 3 belongs to the eruption defined Minopoli 2 (or «Lapillo grigio» of Scherillo, 1955).

Level 2 pumices plot within the area of other products of the first epoch. Only a few pyroclastic deposits are recorded between Pomici Principali and Minopoli 2 tephra (Scherillo, 1955; Scherillo and Franco, 1960; Di Vito *et al.*,

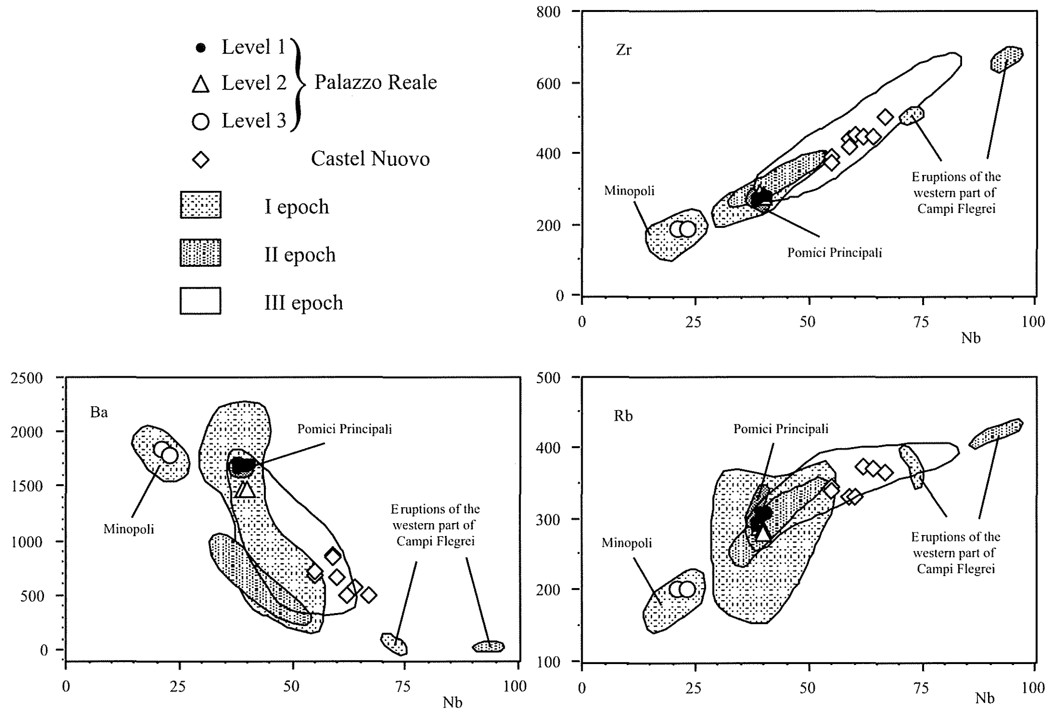

Fig. 4 – Variation diagrams for Zr, Ba and Rb (ppm) versus Nb (ppm) of juvenile fragments from Palazzo Reale and Castel Nuovo. Data fields for various epochs are taken from Lirer *et al.* (1987), Ghiara (1989-1990), D'Antonio *et al.* (1999) and De Vita *et al.* (1999). Eruptions in western part of Campi Flegrei occurred at Archiaverno, Porto Miseno, Baia and Fondi di Baia.

1999): according to sedimentological data and to its chemical composition, this trachyte may be identified as the product of the Soccavo 4 eruption of Di Vito *et al.* (1999) («Seconde Pomici» of Scherillo, 1955). In summary, the data identify the products of Pomici Principali, Soccavo 4 and Minopoli 2 deposits in the Palazzo Reale section, from the bottom upwards, fitting data from other stratigraphic sections (Scherillo, 1955; Di Vito *et al.*, 1999).

Correlation of the stratigraphic section inside Castel Nuovo is more problematic, due to the greater number of pyroclastic levels exposed. A thick paleosoil is covered by the products of at least seven volcanic events. Variation diagrams (fig. 3) show that all the layers of the Castel Nuovo section have compositions quite unlike the products of the first and second epochs, and generally similar to those of the third epoch, with relatively high contents of incompatible elements such as Rb, Zr and Nb.

This character is also clear in frequency histograms (not shown). The Nb content of the products of the first and second epochs is generally lower than 50 ppm, whereas third-epoch rocks have Nb generally higher than 50 ppm and never lower than 30 ppm. It is remarkable that the only eruptions of the first two epochs with more evolved compositions are in the western part of the Campi Flegrei (i.e., Archiaverno, Porto Miseno, Baia, Fondi di Baia) where particular geological conditions hindered the ascent of magma (Orsi *et al.*, 1996; D'Antonio *et al.*, 1999).

During the long period of quiescence that separated the second and third epochs (about 3.5 ka), the liquids which filled the Phlegrean magma chambers, probably representing the residual portions of magmas of older activity (D'Antonio *et al.*, 1999), further evolved mainly by fractional crystallization, involving prevalently alkali feldspar. This process would explain the general higher contents of Zr, Nb, Rb and other elements displayed by the rocks of the last epoch, because these elements are usually incompatible; however, other petrogenetic processes, such as mixing, cannot be excluded (D'Antonio *et al.*, 1999). The lack of mafic rocks emitted during the last epoch seems to support this hypothesis, and also suggests that the Phlegrean magmatic system had probably not been fed with new batches of less evolved magmas since the eruption of Minopoli; these latter products represent more mafic rocks emitted in the last 12 ka. On these grounds, we suggest that the deposits of the Castel Nuovo sequence belong to the third epoch and that the thick paleosoil outcropping at the bottom represents paleosoil B of Di Vito *et al.* (1999). It is not possible to attribute precisely which eruptions occurred in this section.

Di Vito *et al.* (1998) described the volcanological characters of the same section and identified the products of nine eruptions: the first six levels belong to the first epoch (Paradiso, Soccavo 1, Pomici Principali, Soccavo 3, Soccavo 4, Minopoli 2) and two to the third epoch (Agnano Monte Spina, Astroni); the upper part of the sequence is represented by the products of a Vesuvian eruption (Avellino, 3.76± 0.070 ka; Delibrias *et al.*, 1979). The authors relate the reduced thickness of the deposits to sea erosion. The data presented in this work do not match the conclusions drawn by Di Vito *et al.* (1998). Layer C (Pomici Principali Tephra according to Di Vito *et al.*, 1998) and the other levels of this section have a composition distinctly different from that of the Pomici Principali (e.g., lower Zr and Nb, and higher Ba and Sr). Moreover, level C also displays an upward variation in trace element contents that clearly contrasts the homogeneous composition of the Pomici Principali deposit, present about 200 metres down in the excavation below Palazzo Reale. The lack of the Pomici Principali tephra, which represents a good stratigraphic marker, supports our hypothesis that the products of the eruptive events found inside Castel Nuovo refer to the third epoch.

The upper deposit of Castel Nuovo may belong to a Vesuvian eruption. The relevant content of analcime of this deposit, shown by XRD data, is a good indicator of Vesuvian products, generally more SiO_2-undersaturated than the Phlegrean rocks. In this case, analcime represents the transformation product of leucite crystals and/or glass in a sodic environment, related to interaction with coastal brackish water. The chemical data are characterized by high contents of CaO, mainly related to the presence of calcite. This mineral may be related to the precipitation of $CaCO_3$ from water rich in this salt. This hypothesis is supported by the presence of a ferrous spring, also with high Ca contents, near the Castel Nuovo site (spring of Cavalli di Bronzo). In agreement with other stratigraphic reconstructions (e.g., Di Vito *et al.*, 1998), we suggest that these products are related to the Avellino eruption.

Concluding remarks

The stratigraphic section of Palazzo Reale is characterized by pyroclastic deposits belonging, from the base upwards, to the eruptions of Pomici Principali, Soccavo 4 and Minopoli 2 respectively.

The pumice layers of the Pomici Principali have a very uniform trachyphonolitic composition, related to the tapping of a chemically homogeneous magma chamber. However, the presence of very subordinate juvenile latite at the top of a deposit in another section (Rosi and Sbrana, 1987) may indicate that the eruption was triggered by the arrival of more mafic magma in a chamber filled by trachytic magma.

The other section is formed of seven Phlegrean pyroclastic deposits. The uppermost level belongs to a Vesuvian eruption (Avellino). The chemical composition clearly shows that the Phlegrean products belonging to the last epoch of volcanic activity (4.8-3.8 ka B.P.; Di Vito *et al.*, 1999) are characterized by a composition generally richer in incompatible elements than the other post-NYT rocks. This feature may be due to the long period of quiescence between the second and third epochs. During this time, which lasted about 3.5 ka, magmas in the complex Phlegrean magmatic system evolved prevalently by fractional crystallization.

ANALYTICAL TECHNIQUES

Major and trace elements were analysed at Naples (CISAG) with a Philips PW1400 X-Ray fluorescence spectrometer, following the methods described by Melluso *et al.* (1995). Thirty-five international standards were used as calibration analyses. Precision was generally within 1% for SiO_2, TiO_2, Al_2O_3, Fe_2O_3t and CaO, better than 6% for K_2O, ±0.03 wt % for MnO and P_2O_5, and generally better than 5-10% for all trace elements in the observed compositional ranges. Na and Mg were analysed by atomic absorption spectrophotometry at Naples. Typical precision was better than 2% for Mg and better than 6% for Na. L.O.I. (weight loss on ignition) was measured gravimetrically.

Mineralogical investigation was carried out at the Dipartimento di Scienze della Terra, University of Naples, using a PW1730/3710 diffractometer, CuKα radiation and ADP 3.6 software.

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