

# The influence of water on the strength of Neapolitan Yellow Tuff, the most widely used building stone in Naples (Italy)

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## Abstract

Neapolitan Yellow Tuff (NYT) has been used in construction in Naples (Italy) since the Greeks founded the city—then called Neapolis—in the sixth century BCE. We investigate here whether this popular building stone is weaker when saturated with water, an issue important for assessments of weathering damage and monument preservation. To this end, we performed 28 uniaxial compressive strength measurements on dry and water-saturated samples cored from a block of the lithified Upper Member of the NYT. Our experiments show that the strength of the zeolite-rich NYT is systematically reduced when saturated with water (the ratio of wet to dry strength is 0.63). Complementary experiments show that two other common Neapolitan building stones—Piperno Tuff and the grey Campanian Ignimbrite (both facies of the Campanian Ignimbrite deposit devoid of zeolites)—do not weaken when wet. From these data, and previously published data for tuffs around the globe, we conclude that the water-weakening in NYT is a consequence of the presence of abundant zeolites (the block tested herein contains 46 wt.% of zeolites). These data may help explain weathering damage in NYT building stones (due to rainfall, rising damp, and proximity to the sea or water table) and the observed link between rainfall and landslides, rock falls, and sinkhole formation in Naples, and the weathering of other buildings built from zeolite-rich tuffs worldwide.

**Keywords** Zeolites · Uniaxial compressive strength · Porosity · Mercury porosimetry

## Introduction

For millennia, tuffs have been used worldwide as a building stone (Heiken 2006). Cities built on and constructed using tuff span six of the seven continents (all except Antarctica). Tuff has been used as a building material in Naples (Italy; Fig. 1) since the city's birth as Neapolis in the sixth century BCE (e.g., Calcaterra et al. 2000; de'Gennaro et al. 2000a;

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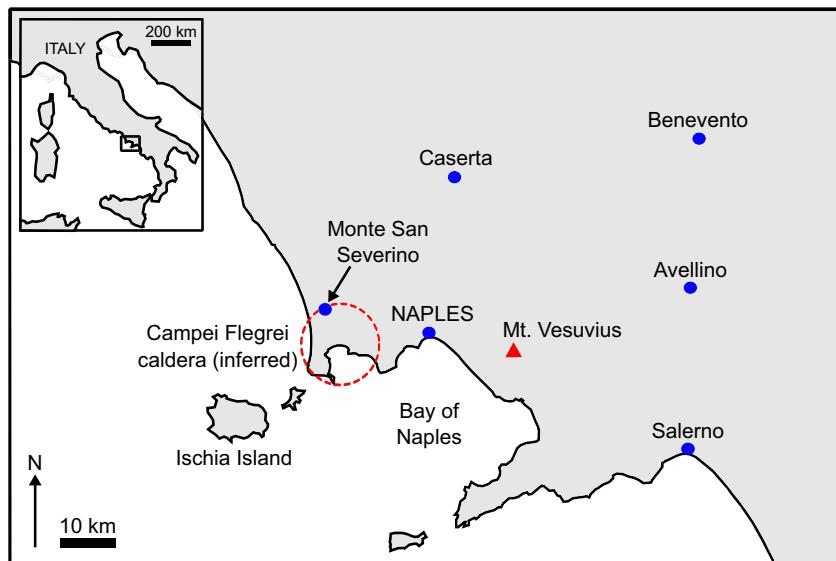
Evangelista et al. 2000a; Colella et al. 2001; Calcaterra et al. 2005; Morra et al. 2010; Aversa et al. 2013; Colella et al. 2017). The most commonly used tuff in Naples is the Neapolitan Yellow Tuff (NYT), the product of a large phreatoplinian eruption from the adjacent Campi Flegrei volcanic district (e.g., Orsi et al. 1992; Scarpati et al. 1993; Wohletz et al. 1995; Orsi et al. 1996; Civetta et al. 1997) about 15,000 years ago (Deino et al. 2004). However, laboratory experiments on tuff show that they are sometimes weaker when saturated with water (e.g., Schultz and Li 1995; Yassaghi et al. 2005; Jackson et al. 2005; Montanaro et al. 2016). The metric “water-weakening”, the ratio of the wet to dry strength of a material, is often used to describe this effect (Zhu et al. 2011), where low values (close to zero) indicate a strong water-weakening effect and values at or close to unity indicate that there is little or no water-weakening. A water-weakening assessment of the NYT is particularly important due to the prevalence of water related weathering typologies seen on buildings in Naples (e.g., de'Gennaro et al. 1993 2000a; Di Benedetto et al. 2015).

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**Fig. 1** Maps showing the location of Naples (inset is a map of Italy). The inferred Campi Flegrei caldera is indicated by the dashed circle, and the main towns with blue dots. The Neapolitan Yellow Tuff (NYT) used in this study was collected from an open quarry at Monte San Severino, on the border of the inferred Campi Flegrei caldera



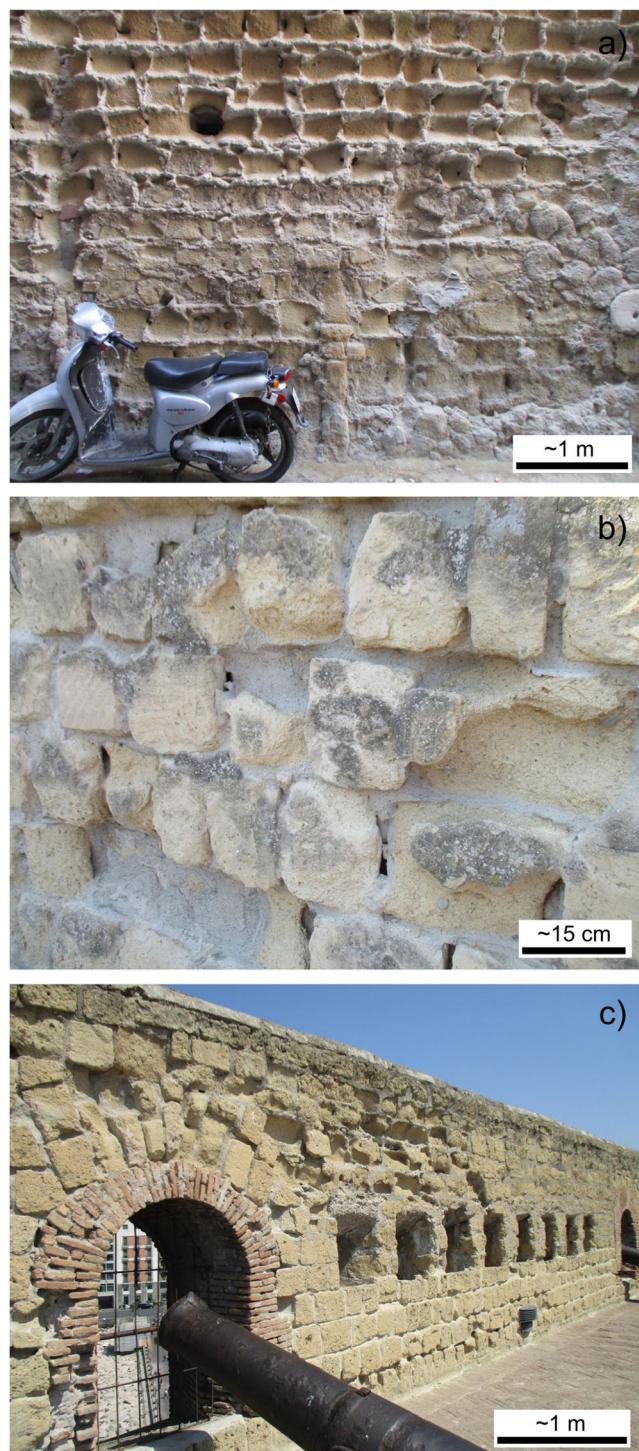
**Fig. 2** Photographs of buildings constructed using Neapolitan Yellow Tuff (NYT) in Naples. (a) Castel dell’Ovo, (b) Castel Nuovo, (c) the church of Santa Chiara, (d) the church of San Domenico Maggiore, (e) the Academy of Fine Arts, and (f) a plastered wall constructed using NYT within the ancient city centre of Naples



The stratigraphy of the NYT is divided into two members: a Lower Member (comprising fall deposits and pyroclastic flow deposits) and an Upper Member (comprising pyroclastic flow deposits) (Scarpati et al. 1993; Cole and Scarpati 1993). The Upper Member is composed of the deposits of a non-turbulent pyroclastic density flow and five low- and high-concentration turbulent pyroclastic density flows (Cole and Scarpati 1993). The Upper Member is variably lithified and is preserved as either unlithified grey “pozzolana” material or a lithified yellow rock (e.g., Scarpati et al. 1993; Cole and Scarpati 1993; de’Gennaro et al. 2000b). The lithified Upper Member has been divided into four texturally distinct units, classified by the size and quantity of lithic and porous juvenile fragments (Colella et al. 2017). The lithified Upper Member of the NYT has not only been used in the construction of monuments such as Castel dell’Ovo, Castel Nuovo, the churches of Santa Chiara and San Domenico Maggiore, and the Academy of Fine Arts, but also in many of the walls and houses within the ancient city centre of Naples (Fig. 2).

The lithified Upper Member of the NYT is a particularly well-studied material, for a number of reasons. First, due to its prevalent use in construction in the Neapolitan area (de’Gennaro et al. 1993; Aversa and Evangelista 1998; de’Gennaro et al. 2000a; Evangelista et al. 2000a; Augenti and Parisi 2010; Nijland et al. 2010; Calderoni et al. 2010; Heap et al. 2012; Di Benedetto et al. 2015; La Russa et al. 2017; Colella et al. 2017). Second, due to the alarming frequency of landslide and rock fall hazards (Calcaterra et al. 2002; Di Martire et al. 2002; Calcaterra et al. 2007; Nocilla et al. 2009) and underground cavity collapse and anthropogenic sinkhole formation (Evangelista et al. 2000b; Hall et al. 2006; Guarino and Nisio 2012; Guarino et al. 2018) associated with the NYT. Third, the NYT contains abundant zeolites, aluminosilicate minerals of commercial, industrial, and environmental importance (de’Gennaro et al., 1990, 2000a; Coppola et al. 2002; Colella 2005). Finally, since NYT is one of the principal lithologies forming the increasingly restless Campi Flegrei caldera (Orsi et al. 1996; Di Vito et al. 1999; Chiodini et al. 2001; Heap et al. 2014; Chiodini et al. 2015; Mayer et al. 2016; Montanaro et al. 2016; Kilburn et al. 2017; Chiodini et al. 2017; Cardellini et al. 2017), a detailed understanding of the physical and mechanical properties of the NYT form an important component of volcanic risk assessment and mitigation.

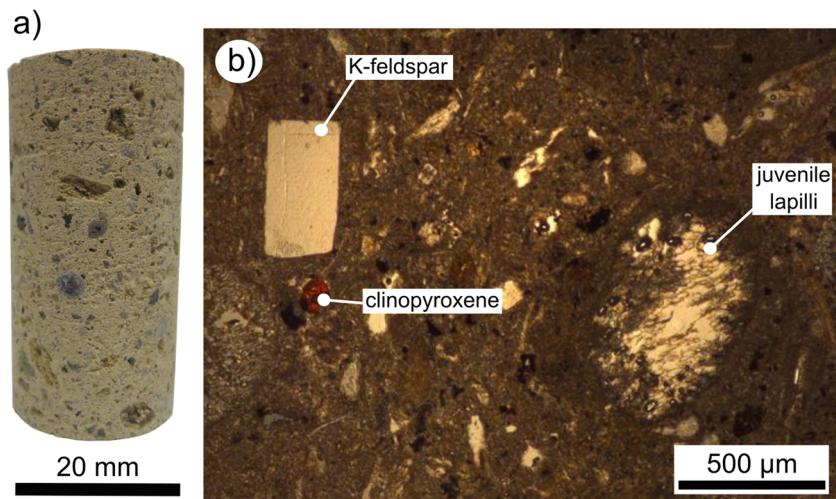
These studies, amongst others, have shown that the lithified Upper Member of the NYT is a heterogeneous trachytic pyroclastic deposit that is characterised by both pyrogenic and authigenic phases (de’Gennaro et al., 1990). It contains variably quantities of porous juvenile lapilli (i.e., pumice) fragments (between ~8 and ~40%) and lithic fragments (between ~7 and ~16%) (Colella et al. 2017). The NYT typically contains a large proportion of plagioclase phenocrysts (between ~14 and ~36 wt.%; Colella et al. 2017), amorphous phases



**Fig. 3** (a) Weathering on a wall constructed using Neapolitan Yellow Tuff (NYT) within the ancient city centre of Naples. (b) and (c) Weathering on NYT walls within the Castel dell’Ovo

(~10 wt.%; Di Benedetto et al. 2015; Colella et al. 2017), and zeolites, namely K-rich phillipsite, chabazite, and analcime (Gatta et al. 2010; Heap et al. 2012; Di Benedetto et al. 2015; Colella et al. 2017). The mean content of zeolites within the NYT can exceed 50 wt.% (de’Gennaro et al., 1990, 2000a;

**Fig. 4** A photograph (a) and an optical photomicrograph (b) of the Neapolitan Yellow Tuff (NYT) used in this study (modified from Heap et al., 2012). A K-feldspar and clinopyroxene phenocryst and a porous juvenile lapilli fragment are labelled on the photomicrograph



Di Benedetto et al. 2015; Colella et al. 2017). Also found within the NYT are subordinate smectite (between 0 and 6 wt.%; Di Benedetto et al. 2015; Colella et al. 2017) and phenocrysts of sanidine, clinopyroxene, biotite, and minor quantities of Ti-magnetite and apatite (Heap et al. 2012; Di Benedetto et al. 2015).

Due to the heterogeneity of the lithified Upper Member of the NYT (e.g., Scarpati et al. 1993; Cole and Scarpati 1993; Colella et al. 2017), its physical properties are equally heterogeneous. For example, its porosity and permeability can range from 0.35 and 0.65 (Colella et al. 2017) and  $10^{-17}$  and  $10^{-13} \text{ m}^2$  (Peluso and Arienzio 2007; Heap et al. 2014; Montanaro et al. 2016), respectively. Reported values of uniaxial compressive strength (UCS) of NYT typically vary between  $\sim 1$  and  $\sim 10$  MPa, although it can be as strong as  $\sim 40$  MPa (Evangelista and Aversa 1994; Hall et al. 2006; Augenti and Parisi 2009; Heap et al. 2012; Montanaro et al. 2016; Colella et al. 2017). Further, and due to its high porosity, triaxial deformation experiments have shown that NYT is compactant (i.e. ductile) even at very low effective pressures ( $< 5$  MPa) and under ambient laboratory temperatures (Aversa and Evangelista 1998; Heap et al. 2014).

The physical and mechanical properties of tuffs are well known to be influenced by exposure to the elements, as recognised by Vitruvius as far back as pre-Christian Rome (Italy), where he wrote: “*There are also many other kinds, such as red and black tuff in Campania, [and] in Umbria, Piceno and in Venetia white, which, indeed, can be cut like wood by means of a serrated or toothed saw. So long as these soft stones are sheltered under plaster they will hold up and do their work but if they are laid bare or exposed in the open air, ice and frost accumulate within them and they crumble apart and dissolve. Also along the sea coast salt eats at them and they dissolve apart; neither do they endure sea tides and spray.*” (from De Architectura 2.7.1–2 as quoted in Jackson et al. 2006). Indeed, and more recently, NYT has been shown

to degrade during salt crystallisation tests (La Russa et al. 2017) and the UCS and indirect tensile strength of zeolite-rich NYT was found to decrease following exposure to the high-temperatures of fire (Heap et al. 2012). However, since the early work of Evangelista (1980), an unpublished report containing experiments that show that the peak strength of NYT is reduced when water-saturated, the water-weakening behaviour of the lithified Upper Member of the NYT has received little attention in the literature. To the authors’ knowledge, only Montanaro et al. (2016) provide a handful of UCS experiments (three dry and three water-saturated) that show that NYT is weaker when saturated with water (dry UCS = 6.1–7.3 MPa; wet UCS = 1.2–2.3 MPa). The lack of a comprehensive study is surprising on two counts. First, deformation experiments on tuffs have highlighted that they are weaker when saturated with water (e.g., Schultz and Li 1995; Yassaghi et al. 2005; Jackson et al. 2005; Montanaro et al. 2016). Second, a survey of weathering typologies in buildings in Naples constructed with NYT found that the most prevalent weathering type was the result of moisture (due to rising damp) and rainfall (de’Gennaro et al. 2000a). This type of weathering results in alveolisation (detachment of lithic and

**Table 1** Quantitative bulk mineralogical composition, determined using X-ray powder diffraction (XRPD), for the Neapolitan Yellow Tuff used in this study

Mineral	Mineral content [wt.%]
Amorphous phase	$36 \pm 5$
K-feldspar	$10 \pm 1$
Biotite	$2 \pm 1$
Clinopyroxene	$3 \pm 1$
Chabazite	$30 \pm 2$
Phillipsite	$16 \pm 2$
Smectite	$3 \pm 1$

porous juvenile fragments), scaling, exfoliation, and disaggregation, as shown in Fig. 3 (see also de'Gennaro et al. 1993 2000a; Di Benedetto et al. 2015). We thus report, herein, on the results of an experimental study that quantifies the water-weakening behaviour of a facies of the NYT often used in construction in the Neapolitan area.

## Experimental material and methods

We performed uniaxial compressive strength (UCS) measurements on cylindrical samples of NYT cored in the same orientation from a single block. The block of NYT (from the lithified yellow Upper Member) was sourced from an open quarry at Monte San Severino, at the boundary of the inferred Campi Flegrei caldera (the same block used in Heap et al.

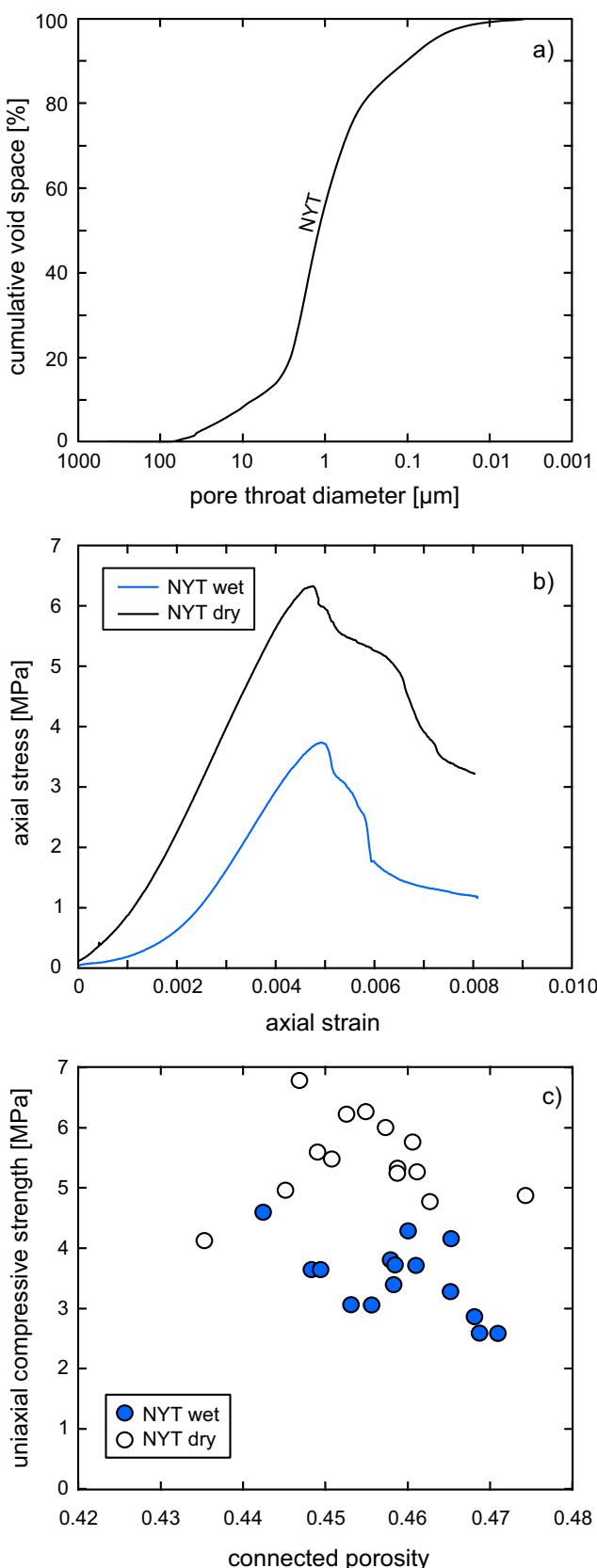
2012 2014; see Fig. 1 for sample location). Importantly, this quarry has supplied dimension stones (natural stone or rock that has been selected and finished to a specific size or shape) for building projects within the Neapolitan area. Due to the presence of centimetric juvenile lapilli, the NYT tested herein is similar to the facies "MC" described by Colella et al. (2017).

A total of 28 samples were cored to a diameter of either 25 or 20 mm and cut and precision-ground to a nominal length of 60 or 40 mm, respectively (a photograph of a 20 mm-diameter sample is provided as Fig. 4a). Samples were cored so as to avoid centimetric juvenile lapilli and lithic fragments. To avoid the washout of juvenile lapilli and the fine fraction, the sample block was first soaked in water and then cored dry (i.e., samples were cored without running water). The prepared cylindrical samples were then washed with water to remove any water-soluble

**Table 2** Summary of the 28 experiments performed on Neapolitan Yellow Tuff (NYT) for this study. Wet—vacuum-saturated in deionised water (see text for details). Dry—dried in a vacuum oven at 40 °C for at least 48 h. The uniaxial compressive strength for a sample of 50 mm

diameter was calculated using the empirical relation given as Eq. (1) (see text for details). The average connected porosities for the samples deformed in the dry and wet condition are 0.456 and 0.459, respectively

Sample	Sample diameter [mm]	Connected porosity	Uniaxial compressive strength [MPa]	Experimental condition	Uniaxial compressive strength (diameter = 50 mm) (Eq. 1) [MPa]
NYT-1	19.83	0.46	3.71	Wet	3.14
NYT-2	19.82	0.46	5.76	Dry	4.88
NYT-3	19.87	0.44	4.60	Wet	3.90
NYT-4	19.77	0.47	4.87	Dry	4.12
NYT-5	19.83	0.47	3.28	Wet	2.78
NYT-6	19.86	0.45	4.96	Dry	4.20
NYT-8	19.84	0.46	5.32	Dry	4.51
NYT-9	19.84	0.45	3.64	Wet	3.08
NYT-10	19.86	0.45	6.26	Dry	5.30
NYT*-1	19.86	0.46	4.29	Wet	3.63
NYT25-1	24.97	0.47	2.87	Wet	2.53
NYT25-2	24.93	0.47	2.59	Wet	2.29
NYT25-3	25.58	0.46	3.73	Wet	3.31
NYT25-4	24.97	0.47	4.16	Wet	3.67
NYT25-5	24.98	0.46	3.40	Wet	3.00
NYT25-6	25.58	0.46	3.81	Wet	3.38
NYT25-7	24.95	0.45	3.07	Wet	2.71
NYT25-8	24.92	0.45	3.65	Wet	3.22
NYT25-9	25.42	0.46	3.06	Wet	2.71
NYT25-10	25.00	0.47	2.58	Wet	2.28
NYT25-11	24.93	0.45	6.23	Dry	5.50
NYT25-12	25.48	0.46	5.22	Dry	4.62
NYT25-13	25.58	0.46	5.26	Dry	4.66
NYT25-14	24.79	0.45	5.59	Dry	4.93
NYT25-15	24.89	0.45	5.48	Dry	4.83
NYT25-16	24.90	0.45	6.78	Dry	5.98
NYT25-17	24.98	0.46	6.00	Dry	5.30
NYT25-19	25.56	0.46	4.77	Dry	4.23



**Fig. 5** (a) Pore throat diameter distribution for the Neapolitan Yellow Tuff (NYT) determined using mercury porosimetry. (b) Representative uniaxial stress-strain curves for a sample of wet (blue curve) and dry (black curve) NYT. (c) Uniaxial compressive strength (UCS) as a function of connected porosity for the NYT. Error associated with transducer precision is within the size of the symbols

grinding fluid and vacuum-dried in an oven for at least 48 h at 40 °C. The connected porosity of each sample was then determined using the skeletal (connected) volume of the sample given by a helium pycnometer (Micromeritics AccuPyc II 1340) and the bulk volume of the sample calculated using the sample dimensions. Finally, the samples were deformed uniaxially at a strain rate of  $1.0 \times 10^{-5} \text{ s}^{-1}$  until macroscopic failure. Thirteen of the samples were deformed “dry” (dried in a vacuum-oven for at least 48 h prior to deformation) and 15 were deformed “wet” (vacuum-saturated in deionised water and deformed in a water bath). The water saturation procedure for the samples deformed in the “wet” condition consisted of two steps:

- (1) the vacuum-dried samples were placed inside a belljar which was then vacuumed for at least 12 h and, finally,
- (2) degassed (using a Venturi siphon with municipal water as the motive fluid) deionised water was introduced into the belljar whilst under vacuum.

A mercury injection test was performed on a small vacuum-dried offcut ( $\sim 3.5 \text{ g}$ ) of NYT using the Micromeritics Autopore IV 9500 at the University of Aberdeen (Scotland). The evacuation pressure and evacuation time were 50  $\mu\text{m Hg}$  and 5 min, respectively, and the mercury filling pressure and equilibration time were 3.59 MPa and 10 s, respectively. The pressure range was 0.69 to 413.69 MPa. Mercury injection data permit the estimation of connected porosity and pore throat size distribution. The mercury injection data were corrected for the “low pressure correction” recommended by the American Section of the International Association for Testing Materials (ASTM D4404-10 2010).

The mineral content of the studied NYT was quantified using X-ray powder diffraction (XRPD). A powder, prepared from the deformed NYT cores and containing 10 wt.% ZnO as internal standard, was ground for 8 min with 10 ml of isopropyl alcohol in a McCrone Micronising Mill using agate cylinder elements. The XRPD analyses were performed on powder mounts using a PW 1800 X-ray diffractometer ( $\text{CuK}\alpha$ , graphite monochromator, 10 mm automatic divergence slit, step-scan  $0.02^\circ$  with 2θ increments per second, counting time one second per increment, 30 mA, 40 kV). The phases in the whole rock powders were quantified using the Rietveld

**Table 3** Summary of the published (including data from this study) wet and dry uniaxial compressive strength of tuffs from around the globe.  $UCS_{dry}$ —dry uniaxial compressive strength;  $UCS_{wet}$ —wet uniaxial compressive strength

Tuff	Outcrop	Connected porosity	$UCS_{dry}$ [MPa]	±	$UCS_{wet}$ [MPa]	±	$\frac{UCS_{wet}}{UCS_{dry}}$	Source	Notes
Anatolian tuff	White Pink	0.39 0.33	0.008 0.021	10.00 16.95	0.88 0.54	3.76 10.89	0.53 1.82	0.376 0.642	Topal and Sözen (2003)
Cappadocian tuff	White Pink	0.28 0.24		8.15 18.23		3.55 10.46	0.436 0.574	Ayday and Göktan (1990)	No zeolites, Smectite, Illite, and Kaolinite present
	Vertical	0.38	0.005	6.53	0.67	2.16	0.34	0.331	Topal and Doyuran (1997)
Horizontal	0.38	0.005	4.87	0.43	0.93	0.29	0.191	Erdogán (1986)	No zeolites, Smectite, Illite, and Kaolinite present
Vertical	0.29		6.50		3.00		0.462	Erguvanlı et al. (1989)	Volcanic glass shards are partly altered to smectite
Vertical	0.29		6.50		3.00		0.462	Tuncay (2009)	Clinoptilolite
Kavak		0.27	3.60		1.10		0.306		
Zelve		0.21	5.00		1.56		0.312		
Cemilköy		0.24	5.00		1.33		0.266		
Kızılıkaya		0.26	4.20		0.83		0.198		
Ortahisar-Ürgüp		0.35	1.20		0.44		0.367		
		0.28	2.20		0.52		0.236		
		0.27	6.30		3.88		0.616		
		0.37	3.40		3.27		0.962		
		0.34	6.60		1.30		0.197		
		0.26	12.90		1.60		0.124		
		0.26	9.70		1.30		0.134		
Calico Hills		0.30	0.015	29.09	3.19	5.34	0.77	Schultz and Li (1995)	Substantially clinoptilolite-rich, but also containing minor erionite, chabazite and phillipsite <sup>1</sup>
		0.38		36.85	4.15	30.40	7.45	Price (1983); Price and Jones (1982)	No zeolites
Karaj tuff		0.40	0.011	4.70	1.20	11.30	2.404	Martin et al. (1994)	Heulandite-clinoptilolite and smectite <sup>2</sup>
		0.10	0.005	121.00	21.00	92.00	14.00	Yassaghi et al. (2005)	No zeolites
		0.13	0.022	92.50	12.50	52.00	3.00		20% clay minerals
		0.13					0.562		
		0.09	0.023	98.50	11.50	64.50	6.50		45% clay minerals
		0.46	0.021	4.85	0.45	2.68	0.88	Marmoni et al. (2017a)	Glass partially replaced by zeolites (incl. Analcime and phillipsite)
		0.21	0.005	33.77	4.03	26.00	0.770	Heidari et al. (2014)	Data not available
		0.03		124.30		78.20	0.679		
		0.24		75.01		29.27	0.390	Behr Jr. (1929)	Contains montmorillonite clay
		0.24		78.92		28.52	0.361		and mordenite (zeolite) <sup>4</sup>
		0.26	0.009	14.90	1.95	6.90	1.03	Yavuz (2012)	Contains smectite and mordenite
		0.37	0.022	22.21	1.47	12.44	0.49	Celik et al. (2014)	Illite and smectite present
Urumieh-Dokhtar tuff		0.36	0.027	19.07	1.69	9.07	0.25	Celik and Egnal (2015)	
Challis tuff		0.24					0.476	Török et al. (2004)	Montmorillonite and other clay minerals
		0.26					0.460	Okubo and Chu (1994)	Contains smectite and mordenite
Alacatı tuff		0.37					0.446		
Ayazini tuff		0.25					0.59		
Seydişehir tuff		0.25					0.565		
Oya tuff		0.25					0.11	Jackson et al. (2005)	Analcime, phillipsite, and chabazite
Tage tuff		0.25					0.480		
Monti Sabatini tuff		0.23							
		0.20							
Tufó Giallo della Prima Porta		0.20							
Tufó Giallo della Via Tibernia		0.15							
Tufó Lionato		0.11							
Lapis Albanus		0.15							
Tufó di Tuseculo		0.14							
Lapis Gabinius		0.13							
Peperino della Via Flaminia		0.35	0.002	43.40	6.21	28.80	3.48	Zhu et al. (2011)	Phillipsite and chabazite
Pisolitico di Trigoria		0.32	0.004				0.500		
Palatino		0.19		39.75			0.683		
Eger-Demjéntuff							0.653		

**Table 3** (continued)

Tuff	Outcrop	Connected porosity	$\pm$	$UCS_{dry}$ [MPa]	$\pm$	$UCS_{wet}$ [MPa]	$\pm$	$\frac{UCS_{wet}}{UCS_{dry}}$	Source	Notes
Tuff from Hungary	Rhyolite tuff	0.40		8.49		3.35		0.395	Vásárhelyi, (pers. Comm.)	
		0.39		4.95		1.59		0.321		
		0.51		3.03		0.74		0.244		
		0.37		7.61		2.60		0.342		
		0.36		6.11		1.37		0.224		
		0.36		5.60		1.91		0.341		
		0.38		7.66		2.24		0.292		
		0.40		4.67		1.74		0.373		
		0.58		2.59		1.15		0.444		
		0.34		8.40		2.76		0.329		
		0.38		4.40		0.87		0.198		
		0.39		5.54		2.02		0.365		
		0.41		3.53		0.55		0.156		
		0.34		5.32		2.21		0.415		
		0.35		7.81		2.94		0.376		
		0.37		3.13		0.63		0.201		
		0.38		5.36		1.20		0.224		
		0.45		2.59		1.18		0.444	Vásárhelyi (2002)	Data not available
		0.30		4.95		1.59		0.321		
		0.32		4.69		1.74		0.371		
		0.29		5.54		2.02		0.365		
		0.27		5.60		1.91		0.341		
		0.30		8.49		3.35		0.395		
		0.30		7.66		2.24		0.292		
		0.30		10.03		7.83		0.781		
		0.28		7.81		2.94		0.376		
		0.29		5.36		1.20		0.224		
		0.29		21.81		21.27		0.975		
		0.15		39.75		26.90		0.677		
		0.20		26.00		20.20		0.78		
		0.15		33.50		27.74		0.83		
		0.17		30.33		22.32		0.74		
		0.16		16.30		8.62		0.53		
		0.07		32.60		21.50		0.66		
		0.11		19.80		10.10		0.51		
		0.08		15.60		11.30		0.72		
		0.14		28.60		19.80		0.69		
		0.27		8.50		8.30		0.98		
		0.20		3.34		2.48		0.74		
		0.30		3.05		1.76		0.58		
		0.22		4.36		3.40		0.78		
		0.31		8.30		14.04		1.69		
		0.24		8.34		12.88		1.54		
		0.00		3.83		3.10		0.81		
		0.09		14.12		13.07		0.93		
		0.09		40.29		18.43		0.46		
		0.03		63.36		53.2		0.84		
		0.49	0.011	6.65	0.65	1.88	0.68	0.28	Montanaro et al. (2016)	
		0.49	0.004	4.56	0.94	2.27	0.97	0.50		Zeolites
	Neapolitan Yellow Tuff La Pietra Tuff 1									

**Table 3** (continued)

Tuff	Outcrop	Connected porosity	$\pm$	$UCS_{dry}$ [MPa]	$\pm$	$UCS_{wet}$ [MPa]	$\pm$	$\frac{UCS_{wet}}{UCS_{dry}}$	Source	Notes
La Pietra Tuff 2 Gairo Tuff	Monte San Severino	0.47 0.46	0.013 0.009	9.74 11.78	0.84 1.17	3.68 4.82	1.32 0.49	0.38 0.41	Phillipsite, chabazite, and smectite	
Neapolitan Yellow Tuff (this study)	Open quarry to the north-west of the town of Caserta (Italy)	0.46	0.017	5.44	0.83	3.81	0.79	0.701	This study	No zeolites or clays present
Grey Campanian Ignimbrite (WGI; this study)	Open quarry in the Neapolitan area (Italy)	0.50	0.005	10.59	1.31	9.94	1.04	0.939		No zeolites or clays present
Piperino tuff (PT; this study)	Open quarry in the Neapolitan area (Italy)	0.51	0.004	3.17	3.29	3.29	1.038		This study	No zeolites or clays present

1. Cejka et al. (2007); Temel and Gündoðdu (1996)
2. Broxton et al. (1993)
3. Levy and O'Neil (1989)
4. Ross and Shannon (1924)
5. Estimated from P\* wet/dry ratio
6. Estimated from P\* wet/dry ratio
7. Wedekind et al. (2013)

program BGMN (Bergmann et al. 1998). To identify the clay minerals, we also separated  $<2\text{ }\mu\text{m}$  fractions by gravitational settling and prepared oriented mounts that were X-rayed in an air-dried and ethylene-glycolated state. Since some of the constituents of the NYT are delicate (juvenile lapilli), and/or may be affected by vacuum-drying (zeolites and clays), we chose to prepare our powdered sample for XRPD analysis using the deformed core samples so that the mineral content determined is representative of the deformed samples, rather than the block prior to sample preparation. Although our samples were prepared with the utmost care, we cannot definitively rule out that their mineral content was slightly modified by the sample preparation procedure.

## Results

### Mineral content and microstructure

The microstructure of the NYT used in this study contains phenocrysts (of K-feldspar, clinopyroxene, and biotite) and juvenile lapilli within a fine-grained matrix (Fig. 4b). Table 1 gives the XRPD analysis, which shows that the main minerals within the NYT are amorphous phases (36 wt.%, Table 1) and two zeolites: chabazite (30 wt.%, Table 1) and phillipsite (16 wt.%, Table 1). The block of NYT also contains 10 wt.% K-feldspar, 3 wt.% clinopyroxene, 3 wt.% smectite, and 2 wt.% biotite (Table 1). The total proportion of zeolites (chabazite and phillipsite) is therefore 46 wt.%. We note that the amorphous phase (36 wt.%, Table 1) measured is likely to contain little residual glass (Colella et al. 2017) and could include an aluminosilicate gel-like component (de'Gennaro and Colella 1989; Colella et al. 2017).

### Experimental data

The NYT studied has an average dry bulk density of  $1240\text{ kg.m}^{-3}$  and an average connected porosity of 0.458 (standard deviation: 0.0079) (Table 2). A connected porosity of 0.446 was determined from the mercury injection data. The pore throat size distribution for NYT is shown in Fig. 5a. These data show that pore throats of diameter  $\geq 10\text{ }\mu\text{m}$  constitute  $\sim 10\%$  of the pores by volume (Fig. 5a). The majority of pores ( $\sim 65\%$ ) have a diameter between 0.3 and 3  $\mu\text{m}$  (Fig. 5a). The average pore throat diameter was determined to be  $0.21\text{ }\mu\text{m}$ .

Representative uniaxial stress-strain curves for dry and wet NYT samples are shown in Fig. 5b, and the UCS is plotted as a function of connected porosity in Fig. 5c (data given in Table 2). The average wet and dry strength was found to be 3.50 and 5.58 MPa, respectively. The ratio of wet to dry strength—a metric commonly used to assess water-weakening in rocks (Zhu et al. 2011)—is 0.63.

**Table 4** Summary of the published wet and dry tensile strengths of tuffs from around the globe.  $\tau_{dry}$ —dry tensile strength;  $\tau_{wet}$ —wet tensile strength

Tuff	Core orientation	Connected porosity	$\pm$	$\tau_{dry}$ [MPa]	$\pm$	$\tau_{wet}$ [MPa]	$\pm$	$\frac{\tau_{wet}}{\tau_{dry}}$	Source	Notes
Eger-Demjén		0.35		0.010	3.30	0.57	2.78	0.36	0.844	Stück et al.
Eger-Tihamér		0.36		0.002	0.81	0.14	0.31	0.08	0.386	(2008)
Weibern tuff		0.43		0.004	1.64	0.22	1.23	0.14	0.754	Fine grained matrix of zeolite minerals
Rochlitz tuff		0.28		0.005	2.42	0.28	1.47	0.26	0.608	Presence of kaolinite
Habichtswald tuff		0.22		0.013	2.68	0.91	2.37	0.6	0.887	Smectite-zeolite matrix
Loseros tuff	X	0.07			6.29		5.82	0.925	Wedeck et al.	Kaolinite, illite, and smectite
	Z	0.07			8.25		6.69	0.811	(2013)	
Cantera Rosa tuff	X	0.41			3.94		2.61	0.662		Smectite and kaolinite
	Z	0.41			4.02		3.00	0.746		
Chiluca tuff	X	0.08			5.13		4.56	0.889		Small amounts of illite and smectite
	Z	0.08			5.61		4.79	0.854		
Gris de los Remedios tuff	X	0.31			2.27		1.39	0.612		Smectites and traces of muscovite/illite
	Z	0.31			2.24		1.58	0.773		
Cantera Formación tuff	X	0.13			10.65		8.23	0.773		Kaolinite and halloysite
	Z	0.13			9.89		8.71	0.881		
Cantera Blanca tuff	X	0.15			6.90		3.99	0.578		Mordenite, clinoptilolite, and montmorillonite
	Z	0.15			5.89		3.11	0.528		
Bufa tuff	X	0.18			6.04		3.65	0.604		Illite and smectite
	Z	0.18			6.95		4.57	0.658		
Tenayocátel tuff	X	0.05			5.43		3.94	0.726		Smectite
	Z	0.05			5.71		4.12	0.722		
Cantera Amarilla tuff	X	0.42			0.99		0.49	0.495		Smectite, kaolinite, and halloysite
	Z	0.42			1.05		0.56	0.533		
Hilbersdorf tuff	X	0.30			3.70		1.14	0.308		Illite
	Z	0.30			4.62		3.10	0.671		

## Discussion

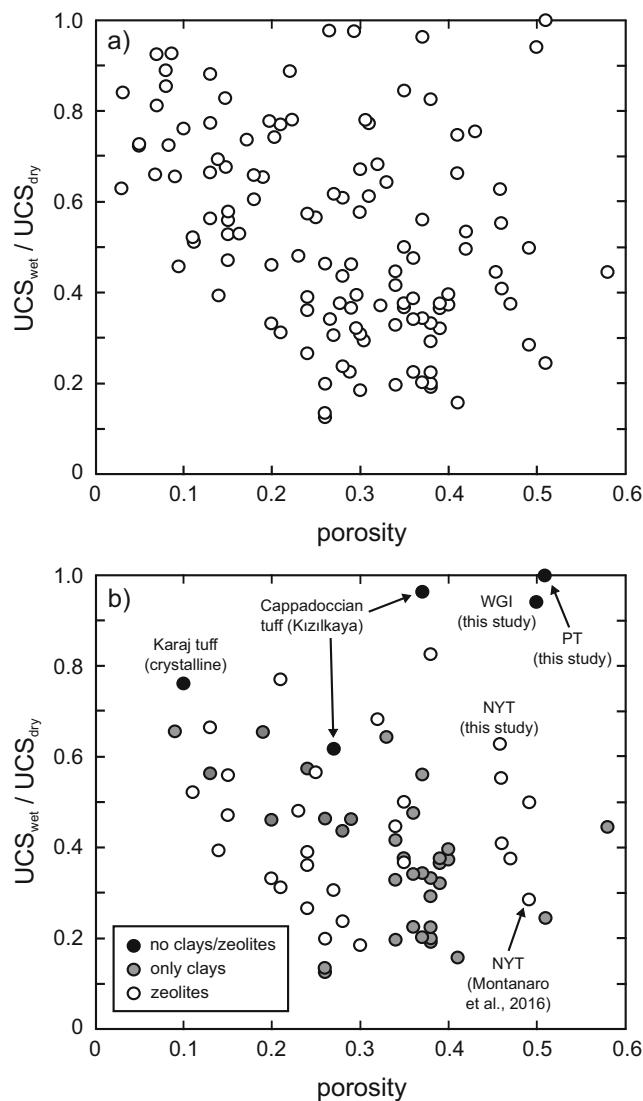
We have performed UCS tests on cylindrical cores of dry and water-saturated NYT either 20 or 25 mm in diameter. Although these diameters are standard in volcanological studies, the strength of engineering materials is typically determined on samples that are 50 mm in diameter. Due to the influence of sample geometry on the UCS (Hawkes and Mellor 1970; Hoek and Brown 1980), we provide here UCS values for 50-mm-diameter core samples using the following empirical relation (Hoek and Brown 1980):

$$UCS = UCS_{50} \left( \frac{50}{d} \right)^{0.18}, \quad (1)$$

where  $UCS$  is the uniaxial compressive strength measured for a cylindrical sample of diameter  $d$  (in mm) and  $UCS_{50}$  is the uniaxial compressive strength of a 50-mm-diameter core sample. The  $UCS_{50}$  values for our experiments are given in Tables 2 and 5. However, although this allows us to better compare our UCS values with those from the engineering

literature, we highlight that the goal of this contribution was to understand whether NYT is weaker when water-saturated. In this case, the metric of interest—the ratio of wet to dry UCS—is independent of sample diameter.

Our data show that the UCS of water-saturated NYT is weaker than dry NYT (Fig. 5c). These data are in accordance with tuffs sourced from Italy and elsewhere. For example, studies have shown that the tuffs from the Cappadocia (Erdoğan 1986; Erguvanlı et al. 1989; Topal and Doyuran 1997; Tuncay 2009; Erguler and Ulusay 2009) and Afyonkarahisar (Çelik et al. 2014; Çelik and Ergul 2015) regions of Turkey, tuffs from different locations in Hungary (Vásárhelyi 2002), and tuffs from Rome (Jackson et al. 2005) and the Neapolitan area (Montanaro et al. 2016; Marmoni et al. 2017a) are weaker when wet. To test the hypothesis that the presence of zeolites and/or clays is responsible for the observed water-weakening in tuffs, we have collated the available published data on the wet versus dry compressive (Table 3) and tensile (Table 4) strength of tuffs from around the world (Fig. 6). All the data are presented in Fig. 6a, and Fig. 6b shows only UCS data for which the composition is known. The data in Fig. 6b have been divided into three



**Fig. 6** (a) Water-weakening (ratio of wet to dry strength) as a function of porosity for tuffs all over the world. (b) Ratio of wet to dry uniaxial compressive strength as a function of porosity (data for which the composition is known). Data are in three groups (1) tuffs that contain zeolites (white circles), (2) tuffs that contain clays but no zeolites (grey circles), and (3) tuffs that contain neither zeolites nor clays (black circles). Data from: this study, Behre Jr. (1929), Price (1983), Price and Jones (1982), Erdogan (1986), Erguvanlı et al. (1989), Ayday and Göktan (1990), Martin et al. (1994), Okubo and Chu (1994), Schultz and Li (1995), Topal and Doyuran (1997), Vásárhelyi (2002), Topal and Sözmen (2003), Török et al. (2004), Yassaghi et al. (2005), Jackson et al. (2005), Tuncay (2009), Stück et al. (2008), Erguler and Ulusay (2009), Zhu et al. (2011), Heidari et al. (2014), Wedekind et al. (2013), Çelik et al. (2014), Çelik and Ergul (2015), Montanaro et al. (2016), Marmoni et al. (2017a), Marmoni et al. (2017b), and Vásárhelyi (pers. comm.)

groups: (1) tuffs that contain zeolites, (2) tuffs that contain clays but no zeolites, and (3) tuffs that contain neither zeolites nor clays.

To complement these data, we performed ancillary experiments on two tuffs that contain no zeolites or clays—the grey Campanian Ignimbrite (welded grey ignimbrite, WGI) and the

Piperno Tuff (PT). Both rocks are facies of the Campanian Ignimbrite deposit (e.g., Barberi et al. 1978; Rosi et al. 1996; Fedele et al. 2016) and have been used in construction within the Neapolitan area (e.g., Calcaterra et al. 2000; de'Gennaro et al. 2000a; Calcaterra et al. 2005; Morra et al. 2010). The use of PT is particularly widespread in the ancient city centre of Naples, the church of Gesù Nuovo providing a spectacular example (Fig. 7). Piperno Tuff was also used to construct the corner towers of Castel Nuovo (Fig. 2b). Cylindrical samples (20 mm in diameter and nominally 40 mm in length) were prepared from both the WGI block described in Heap et al. (2012 2014) and the PT block described in Heap et al. (2012), as described in the methods section above. The WGI samples tested contain hypidiomorphic phenocrysts of alkali feldspar with minor clinopyroxene within a matrix composed of microlites of alkali feldspar, Ti-magnetite, and apatite, as well as well-sorted glass shards with occasional accretionary ash clots and porous lapilli fragments (Heap et al. 2012). Piperno Tuff is characterised by a eutaxitic texture with black flattened scoriae and phenocrysts of alkali feldspar and clinopyroxene set within a light grey matrix of well-sorted glass shards and microlites of alkali feldspar and Ti-magnetite (Heap et al. 2012). Importantly, no zeolites or clays are present within these blocks (see XRD data presented in Heap et al. 2012). The connected porosities of the WGI and PT samples were first determined; the samples were then deformed in either the dry or wet condition (as described in the methods section above). The results of these experiments are summarised in Table 5. The ratio of wet to dry strength in WGI and PT is 0.939 and 1.038, respectively (Fig. 6b; Table 3). In other words, based on these data, WGI and PT are not weaker in the presence of water.

Figure 6b suggests that the presence of zeolites and clays promote water-weakening in tuffs, although firm conclusions cannot be drawn due to the paucity of data for zeolite-free tuff. The four samples of zeolite-free tuff (Karaj (crystalline), Cappadocian (Kızılkaya), the WGI, and the PT) show consistently high ratios of  $UCS_{wet}/UCS_{dry}$ —between ~0.6 and ~1.0 (Fig. 6b; Table 3). By contrast, zeolite- and clay-bearing tuffs have average  $UCS_{wet}/UCS_{dry}$  ratios of 0.54 and 0.37, respectively (Fig. 6b; Table 3). We therefore conclude that the water-weakening in NYT is the result of the presence of abundant zeolites (46 wt.% in total; Table 1), although the influence of subordinate clay (3 wt.%; Table 1), thought to promote water-weakening in sandstones (Dyke and Dobereiner 1991; Schmitt et al. 1994; Demarco et al. 2007; Shakoor and Barefield 2009), cannot be discounted. We attribute the observed weakening in the presence of water to the hydric expansion of zeolites and clays (e.g., Nijland et al. 2010; Wedekind et al. 2013; López-Doncel et al. 2013). However, based on the available data, we cannot definitively rule out the influence of porosity type (pores versus

**Fig. 7** (a) Photograph of the church of Gesù Nuovo in Naples. (b) Photograph of front of the church of Gesù Nuovo showing the pyramid-shaped bossage constructed using Piperno Tuff



microcracks), pore shape, average pore size, and pore size distribution, amongst others, on the water-weakening behaviour of tuffs. Indeed, Wedekind et al. (2013) found a correlation between microporosity, average pore radius, and moisture expansion for a variety of tuffs from Mexico, Germany, and Hungary.

We also highlight that, in our study, we compare the strength of dry and fully saturated samples. In reality, it is unlikely that building stones will be fully saturated with water. However, experimental studies have shown that even low levels of water saturation can result in measurable water-weakening in tuffs (Kleb and Vásárhelyi 2003; Çelik and Ergül 2015). For example, Çelik and Ergül (2015) found that immersion in water for 1 h was sufficient to reduce the strength of tuff by ~32%. Water-weakening at low levels of water saturation has also been observed in clay-rich sandstones (Dyke and Dobereiner 1991; Schmitt et al. 1994; Demarco et al. 2007; Shakoor and Barefield 2009). Therefore, we consider our conclusions, drawn from experiments on dry and fully saturated samples, are relevant for monuments and buildings constructed using NYT. We further note that we have only tested one facies of the heterogeneous

lithified Upper Member of the NYT (Colella et al. 2017). However, yellow-coloured tuffs associated with more recent (post-NYT) eruptions at Campi Flegrei (Gauro and La Pietra Tuffs) also show water-weakening (Montanaro et al. 2016; Table 3). Importantly, these tuffs are texturally different to the facies studied herein. Indeed, one of the La Pietra Tuffs contained very few lapilli-sized lithic and porous juvenile fragments (similar to the “NP” end-member facies of the NYT reported in Colella et al. 2017). Based on these data, we expect the NYT facies that are texturally different to that studied herein will also be weaker when wet (as long as they contain zeolites), although more experiments should now be performed to test this hypothesis.

## Conclusions

We have shown that a block of the lithified Upper Member of the NYT, often used in construction within the Neapolitan region of Italy, is weaker when water-saturated (Fig. 5c). Compiled data on the wet and dry strength of tuffs from across the globe suggest that the cause of the water-weakening is the

**Table 5** Summary of the experiments performed on Piperno Tuff (labelled “PIP”) and the grey Campanian Ignimbrite (labelled “CI”) for this study. Wet—vacuum-saturated in deionised water (see text for details). Dry—dried in a vacuum oven at 40 °C for at least 48 h. The uniaxial compressive strength for a sample of 50 mm diameter was calculated using the empirical relation given as Eq. (1) (see text for details)

Sample	Sample diameter [mm]	Connected porosity	Uniaxial compressive strength [MPa]	Experimental condition	Uniaxial compressive strength (diameter = 50 mm) (Eq. 1) [MPa]
PIP-1	20.26	0.51	3.17	Dry	2.69
PIP-2	20.29	0.50	3.29	Wet	2.80
CI-4	19.85	0.50	10.97	Wet	9.29
CI-9	19.79	0.50	9.54	Wet	8.07
CI-10	19.82	0.50	9.59	Wet	8.12
CI-11	19.83	0.50	9.65	Wet	8.17
CI-13	19.81	0.50	10.88	Dry	9.21
CI-19	19.81	0.50	10.17	Dry	8.61
CI-20	19.83	0.50	11.05	Dry	9.36
CI-21	19.83	0.50	8.95	Dry	7.58
CI-22	19.84	0.50	11.90	Dry	10.08
CI*-2	19.83	0.50	10.94	Wet	9.26

due to the presence of zeolites (Fig. 6b). Water-weakening in the zeolite-rich NYT may help explain the widespread weathering observed in Naples due to moisture (as a result of rising damp) and rainfall (Fig. 3; de'Gennaro et al. 1993 2000a; Di Benedetto et al. 2015) and the apparent link between rainfall and landslide and rock fall hazards (Calcaterra et al. 2002; Di Martire et al. 2012; Calcaterra et al. 2007; Nocilla et al. 2009) and sinkhole formation (Guarino and Nisio 2012). We additionally conclude that the buildings constructed using zeolite-free tuffs, such as the church of Gesù Nuovo (Fig. 7), will be less prone to weathering associated with moisture and rainfall. This latter hypothesis is supported by the observation that, while the WGI is only subject to physical weathering, the zeolitised facies of the Campanian Ignimbrite is more affected by chemical action (de'Gennaro et al. 1995). We anticipate that the implications of this study will be important not only for building and monument preservation in Naples, but also in other cities worldwide constructed using tuff.

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