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ABSTRACT
Tuff has been extensively used as a building material in volcanically and tectonically active areas over many centuries, despite its inherent low strength. A common and unfortunate secondary hazard accompanying both major volcanic eruptions and tectonic earthquakes is the initiation of catastrophic fires. Here we report new experimental results on the influence of high temperatures on the strength of three tuffs that are commonly used for building in the Neapolitan region of Italy. Our results show that a reduction in strength was only observed for one tuff; the other two were unaffected by high temperatures. The cause of this strength discrepancy was found to be a product of the initial mineralogical composition, or more specifically, the presence of thermally unstable zeolites within the initial rock matrix. The implications of these data are that, in the event of fire, only the stability of buildings or structures built from tuff containing thermally unstable zeolites will be reduced. Unfortunately, this includes the most widespread material in Neapolitan architecture. We recommend that this knowledge should be considered during fire hazard mitigation in the Neapolitan area and that other tuffs used in construction worldwide should be tested in a similar way to assess their fire resistance.

INTRODUCTION
Tuff is a very weak geomaterial (Schultz and Li, 1995; Hall et al., 2006; Tuccimei et al., 2010; Zhu et al., 2011). It has nevertheless been extensively used as a building material in volcanically and tectonically active areas (e.g., in Naples and Rome, Italy) due to the combination of local availability and its easy workability. Given its widespread use, we examined the high-temperature stability of tuff in the event of fire; catastrophic fire (especially in urban areas) is also a common secondary hazard accompanying major volcanic eruptions and tectonic earthquakes. Here we report new experimental results on the influence of high temperatures on the strength of three tuffs from the Campanian region of Italy.

MATERIALS AND METHODS
We performed uniaxial compressive and indirect tensile strength tests on thermally stressed samples of Neapolitan Yellow Tuff (NYT), gray Campanian Ignimbrite (welded gray ignimbrite, WGI), and Piperno Tuff (PT). The tuffs were formed during large explosive eruptions from the Campi Flegrei caldera (Orsi et al., 1996; de Gennaro and Langella, 1996; de Gennaro et al., 2000), located a few kilometers west of the city of Naples, and have all been used in construction throughout the Neapolitan area (see Morra et al., 2010, and references therein). Our sample materials were collected from open quarries (that supply material for construction) within the Campanian area. Prior to experimentation, the “as-received” materials (i.e., samples that have undergone no heating) were characterized using optical microscopy (carried out using a Leica DM2500 microscope; see GSA Data Repository1) and X-ray diffraction (XRD) (carried out using a Stoe Kristallograph diffractometer; see the Data Repository). NYT, a trachytic pyroclastic deposit characterized by both pyrogenic and authigenic phases (de Gennaro et al., 2000), was found to contain phenocrysts of sandine, plagioclase, clinopyroxene, biotite, and minor amounts of titaniferous magnetite and apatite within a matrix of lapilli and glass shard ash (Fig. 1A). The glass shards frequently contain microscopic vesicles, as well as nanosopic crystals. Xenoliths of fine-grained gabbro (altered and near pristine) were also found. XRD pattern analysis confirmed the presence of the above-mentioned crystals and also indicated the presence of sesquicarbonate and three zeolites, phillipsite, chabazite, and analcime (Fig. 2A). The presence of these zeolites in NYT has been reported in previous studies, and their mean content can exceed 50 wt% (de Gennaro et al., 1990, 2000). The WGI, feldspatized by authigenic mineralization processes, is made up of reversely graded black scoriae embedded in an ash matrix with subordinate lithics and crystals (Cappelletti et al., 2003). The WGI was found to contain hypidiomorphic phenocrysts of alkali feldspars with minor amounts of clinopyroxene, as well as microlites of alkali feldspar, titaniferous magnetite, and apatite, giving the matrix a trachytic appearance (Fig. 1E). The matrix comprises well-sorted glass shards with occasional accretionary ash clots and porous lapilli fragments (Fig. 1F). PT is characterized by a eutaxitic texture with black flattened scoriae set in a light gray matrix (Calceterra et al., 2000), and was found to contain hypidiomorphic phenocrysts of alkali feldspars with minor amounts of clinopyroxene. The microlites are not well developed and tend to be fragments of alkali feldspar. Titaniferous magnetite and apatite are present as accessory minerals. The matrix comprises well-sorted glass shards surrounding porous lapilli fragments (Fig. 1H). NYT, WGI, and PT contain average porosities of 44%, 49%, and 48%, respectively (measured using an AccuPyc II 1340 helium pycnometer).

Experimental samples comprised cylindrical cores 25 mm in diameter by 75 mm long (resulting in a length:diameter ratio of 3:1) for uniaxial compressive strength tests, and discs 40 mm in diameter by 20 mm thick for indirect tensile strength tests (within the thickness-diameter ratio suggested by the International Society for Rock Mechanics [ISRM, 1978]). Prior to strength testing, samples were either (1) held at ambient temperature, or (2) thermally stressed to predetermined temperatures of 100, 200, 300, 500, or 750 °C. Thermal stressing was achieved by heating the sample to the target temperature at a rate of 1 °C/min without load, holding the temperature constant for 60 min, and then cooling at the same rate. Strength tests were then performed on all samples using special testing jigs mounted in a servo-controlled uniaxial load frame. In our uniaxial compression tests, core samples were loaded at a constant strain rate of 1.0 × 10−4 s−1 until failure. Indirect tensile tests were conducted using the Brazil-disc technique (ISRM, 1978), in which discs are loaded diametrically in compression to produce a maximum tensile stress at their center. Indirect tensile strengths were then calculated using standard rock mechanics relationships (ISRM, 1978).

RESULTS AND DISCUSSION
Results demonstrate that, whereas the strength of NYT decreased with thermal stressing, the strengths of WGI and PT remained unaffected.
and chabazite undergo reversible hydration at 350 °C; and at 900 °C, irreversible dehydration at 240 °C; phillipsite breaks down during dehydration.

Detailed studies on the thermal decomposition of the zeolites in NYT have highlighted that analcime irreversibly loses water and chabazite and phillipsite undergo a partial reversible dehydration.

Some areas show the presence of foamed glass as much as 1 mm wide (Figs. 3A and 3B). The compressive strength and indirect tensile strength of NYT were reduced by 80% (from 3.4 to 0.7 MPa) and 90% (from 1 to 0.1 MPa), respectively. The gradual degradation of strength with thermal stressing in NYT is also illustrated in the stress-strain curves of Figure 3C.

To investigate the cause of this discrepancy in strength reduction, we first performed thermogravimetric analysis (carried out using a Netzsch STA 449 C thermobalance apparatus; see the Data Repository) on all three samples (Fig. 3D). Thermogravimetric analysis permits us to evaluate the amount of hydrated minerals contained within the three tuffs. Figure 3D shows that, at 1000 °C, NYT had lost 18% of its initial mass, whereas WGI and PT had only lost ~2%. It follows that the more mass lost during heating, the more hydrated minerals contained within the material (see also de Gennaro and Colella, 1989). The nature of these hydrated minerals was further investigated using a combination of XRD and optical microscopy on samples thermally stressed to 1000 °C, to be compared with our observations of the as-received materials. Thermally stressing the NYT to 1000 °C resulted in the disintegration of the matrix, revealed by the presence of distributed and nonpreferentially oriented 1–100-µm-wide microcracks (Fig. 1B).

The implications of these data are that, in the event of fire, the stability of buildings or structures built from NYT will deteriorate considerably. One of the most infamous fires in a building constructed from NYT is that of the Church of Santa Chiara, Naples (built between A.D. 1310 and 1340), in 1943. The fire, initiated after an air raid attack during the Second World War accidentally hit the church, roared for 10 days and almost destroyed the church entirely. Restoration work on the church, back to its original Gothic style, was completed in 1953.

Grey Campanian Ignimbrite (WGI)

Piperno Tuff (PT)

Figure 1. A: Optical microscopy photomicrograph (OMP) of “as-received” Neapolitan Yellow Tuff (NYT). B, C, D: OMPs of samples of NYT thermally stressed to 1000 °C. E, F: OMPs of Campanian Ignimbrite (welded gray ignimbrite, WGI). G: OMP of WGI thermally stressed to 1000 °C. H: OMP of Piperno Tuff (PT). I: OMP of PT thermally stressed to 1000 °C. See text for details.
Figure 2. X-ray diffraction (XRD) patterns. A: Neapolitan Yellow Tuff. Only hydrated minerals and biotite (Bt) are labeled in A. Ph—phil-lipsite; Ch—chabazite; An—analcite; Se—segelerite. B: Gray Campanian Ignimbrite (welded gray ignimbrite, WGI). C: Piperno Tuff. Panels show both “as-received” XRD patterns (black lines) and XRD patterns for samples thermally stressed to 1000 °C (gray lines).

Figure 3. A: Influence of thermal stressing on uniaxial compressive strength (one sample per temperature). NYT—Neapolitan Yellow Tuff; WGI—welded grayCampanian Ignimbrite; PT—Piperno Tuff. B: Influence of thermal stressing on indirect tensile strength (average of two samples per temperature). C: Stress-strain curves for constant strain rate uniaxial compressive tests on samples of thermally stressed NYT. Temperature next to each curve indicates thermal stressing temperature for that sample. D: Mass loss with temperature for each sample, by means of thermogravimetric analysis.
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