Depositional properties and geochemistry of Holocene perched springline tufa deposits and associated spring waters: a case study from the Denizli Province, Western Turkey

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Depositional properties and geochemistry of Holocene perched springline tufa deposits and associated spring waters: a case study from the Denizli Province, Western Turkey

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Abstract: The Güney waterfall area is a perched springline tufa site developed on the southeast slope of the Büyük Menderes River near Güney town, in the Denizli province, Western Turkey. The site is 12 km away from Güney and 72 km from the city centre of Denizli. The spring waters emerge from the boundary between Palaeozoic marble and micaschist and precipitated tufa deposits downslope at the altitudes ranging from 220 to 400 metres. The tufa deposits cover an area of about 20 hectares. Flat upper surfaces of the deposits are indicative of mature stage. The waters are of the Ca–HCO_3 type and supersaturated with respect to $CaCO_3$. The stable isotope values of the spring waters are −49.94 for δ^2H and −7.15 for δ^{18}O. The δ^{13}C and δ^{18}O values of active and passive tufa samples are in the range from −9.13 to −6.0‰, and from −8.44 to −7.40‰, respectively. These isotopic values are typical for fresh water tufa. The passive tufas give the ^{14}C age in the range from 2000 to 5800 yr BP. According to the ^{14}C age data, passive tufas are not older than Holocene. The stable isotope composition is similar south European examples.

Tufa and travertine are common carbonate deposits in Quaternary and present-day depositional systems (Chafetz & Folk 1984; Ford & Pedley 1996; Guo & Riding 1998; Arenas *et al.* 2000; Horvatinčić *et al.* 2000; Glover & Robertson 2003; Bonny & Jones 2003) and are known from Neogene and older successions (Arp 1995; Evans 1999; Cole *et al.* 2004). In this paper, 'tufa' was considered as subaerial deposits produced from ambient temperature waters and contains typically the remains of micro- and macrophytes, invertebrates and bacteria (Ford & Pedley 1996; Arenas *et al*. 2000; Pedley *et al.* 2003). On the other hand, travertine is hydrothermal in origin (Chafetz & Folk 1984; Guo & Riding 1998; Minissale *et al.* 2002).

Ford & Pedley (1996) divided tufa deposits into: (1) perched springline, (2) fluvial; (3) lacustrine; and (4) paludal depositional systems. Subsequently, Pedley (2009) added the cascade model. Perched springline tufa deposits, which occur on valley slopes in mountainous or hilly countries, are part of the tufa depositional continuum (Ford & Pedley 1996; Pedley 2009; Pedley *et al.* 2003). These deposits have been used as indicators of palaeohydrogeological evolution in karstic massifs and used to evaluate climatic change in the Mediterranean areas (Martín-Algarra *et al.* 2003). Although outlines of these deposits have been presented previously in Pedley (1990), Ford & Pedley (1996) and Pedley *et al.* (2003), there are few well-documented sites (Andreo *et al.* 1999; Martín-Algarra *et al.* 2003; Anzalone *et al.* 2007).

Although, the Denizli province in the western Turkey is well-known for its travertine deposits and associated geothermal fields (Altunel & Hancock 1993; Gökgöz 1998; Şimşek *et al.* 2000; Özkul *et al.* 2002; Şimşek 2003), there are also a few tufa sites (Ceylan 2000; Horvatinčić *et al.* 2005). In this study, the depositional features and geochemistry of a unique example of perched springline tufa deposits and accompanying spring waters near the Güney town, Denizli, SW Turkey are examined.

Location and geological setting

The site is located on the SE slope of the Büyük Menderes river valley near the town of Güney in the NW part of the Denizli basin, western Turkey (Figs 1 & 2). The site is 12 km from Güney and 72 km north of the city of Denizli. Based on long-term data, the mean annual temperature and the rainfall are about 13.5 °C and 548.8 mm, respectively. The tufa deposits rest on marble and schist of the Palaeozoic metamorphic bedrock that belong to the Menderes masif (Bozkurt & Oberhänsli 2001; Erdoğan & Güngör 2004). The bedrock is unconformably overlain by a late Miocene lacustrine succession (Koçyiğit 2005; Kaymakçı 2006; Alçiçek *et al.* 2007) at higher altitude of 900 m where the Cindere

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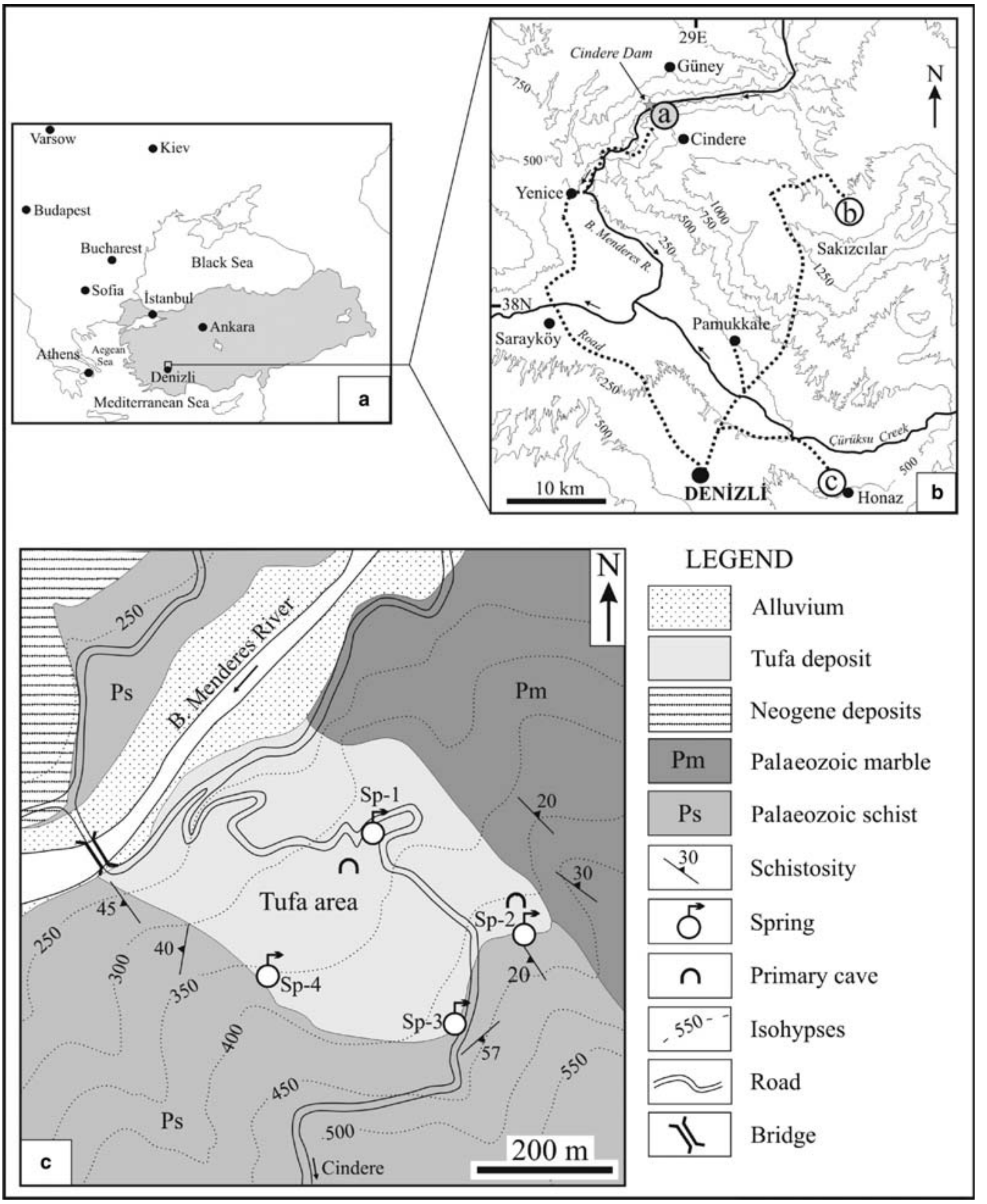

Fig. 1. (**a**) Geographical setting of the Denizli province in Turkey; (**b**) Location of the Güney springline tufa site (a) and other two tufa sites (b: Sakızcılar and c: Honaz) in the province and (**c**) Local geological map of the Güney springline tufa site. Sp-1, 2, 3 and 4 are spring resurgences.

village located (Fig. 2). The tufa deposits cover an area of about 20 hectares.

A road goes up through the tufa deposits from the river bed towards Cindere (Fig. 1c). The Güney waterfall site is an area of unique geological/natural heritage that is visited by many people, especially during spring and summer seasons. There are mainly four springs and numerous seeps that emerge from the metamorphic bedrock that has been fractured intensely. The spring waters have formed coalescent tufa bodies that occur at elevations between 220–400 m above the Büyük Menderes river bed (Fig. 1c).

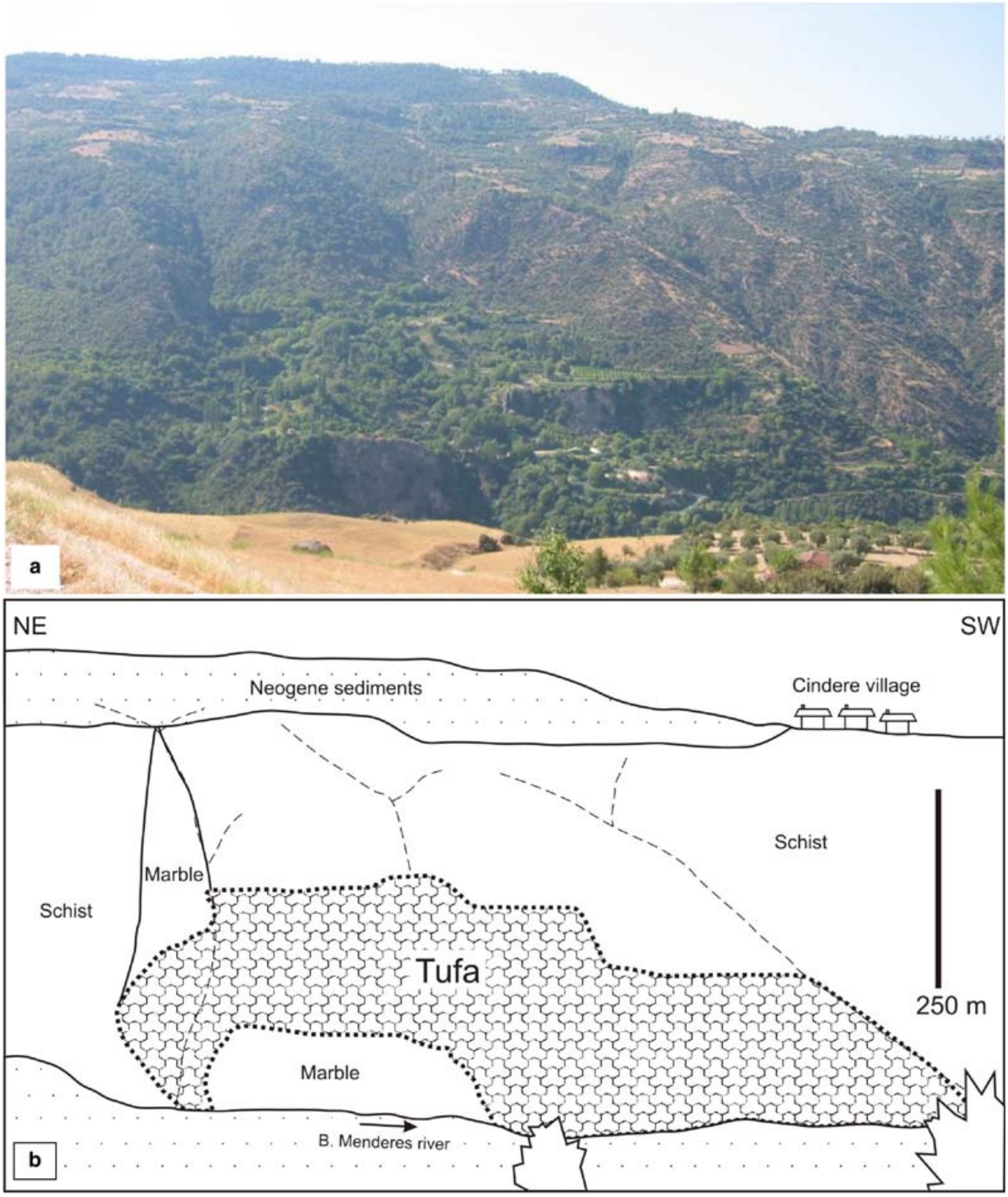

Fig. 2. Panaromic view (**a**) and drawing interpretation (**b**) of the Güney perched springline tufa site. The late Miocene lacustrine sediments rest unconformably on the bedrock composed of schist and marble belong to Menderes massif of Palaeozoic age around Cindere village.

Methods

Fieldwork

The Güney tufa site was visited seasonally from July 2003 to December 2005. During the early stages of the study, geological and depositional features of the tufa site were investigated and a local geological map was prepared (Fig. 1c). Some physicochemical analyses and measurements of the waters were carried out at several points during midday along the flow paths in order to monitor the seasonal variations at physical and chemical parameters.

Temperature and pH values were measured using a HACH Sension 2 pH meter at the time of sampling. Electrical conductivity was measured

Fig. 3. Field view of the active waterfall and lobe-top terrace areas developed in front of Sp-4. The flat lobe-top terrace is presently used as an agricultural area by local people. The water of Sp-4 flowing through an elevated channel (dotted sinuous line) on the terrace area reaches to the spill-over point of the active waterfall-top. A primary cave (P.C., arrowed) has developed within the active waterfall tufa body.

with a HACH Sension 5 conductivity meter. CO_2 and HCO_3 were determined volumetrically by titration using NaOH and H_2SO_4, respectively. Water samples were collected for chemical analysis and each water sample consists of two 500 ml polyethylene bottles. One of the bottles was acidified with ultra pure HNO_3 ($pH < 2$) after filtering with 0.45 μm cellulose membrane filters for the determination of cations and the other was unacidified for anion analyses which is kept at a temperature equal to lower than +4 °C.

Both active and passive tufa samples were collected for mineralogical, petrographical and geochemical analysis (including major and trace elements, SEM investigations and isotope composition).

Laboratory work

Major constituents of water were determined at the geochemistry laboratory of the Geological Engineering Department at Pamukkale University. Ca, Mg, Na and K concentrations of the water samples were determined using a UNICAM atomic absorption spectrometer. Cl and SO_4 were determined by a HACH DR/4000 visible spectrophotometer. The stable isotope (δ^2H, δ^{18}O and δ^{13}C in DIC of water) and δ^3H analyses of some waters were performed at the laboratory of the Faculty of Earth and Life Science in Vrije University (Amsterdam) and at the Geological Engineering Department in Hacettepe University (Ankara), respectively. Mineral saturation indices of hydrothermal minerals were calculated using the PHREEQC computer code (Parkhurst & Appelo 1999).

The tufa samples were examined by optical microscope in thin section and some selected samples were studied on a scanning electron microscope (SEM; Jeol JSM 6490 LV). SEM investigations were performed at Turkish Petroleum Corporation (TPAO) in Ankara. The mineralogy of the tufa samples was determined by X-ray diffraction (XRD) using a Phillips PW 1729 diffractometer at the Geological Engineering Department, Hacettepe University. Major and trace elements

Fig. 4. Field photographs of the Güney perched springline tufa site. (**a**) The active waterfall area; (**b**) Frontal part of the extinct waterfall area adjacent to active part; (**c**, **d**) Close views of the active waterfall front accompanied by overhanged bryophyte (moss) curtains and pouring water column; (**e**) Lower slope tufa deposits exposed at the extinct waterfall foot along the roadside section, note that the steep inactive waterfall tufa facing downslope; (**f**) An inside view of the primary cave located behind the tufa body of the active waterfall. A shallow pool took place at the bottom and the cave walls were coated by speleothems, note the trace of highstand water level above present water surface.

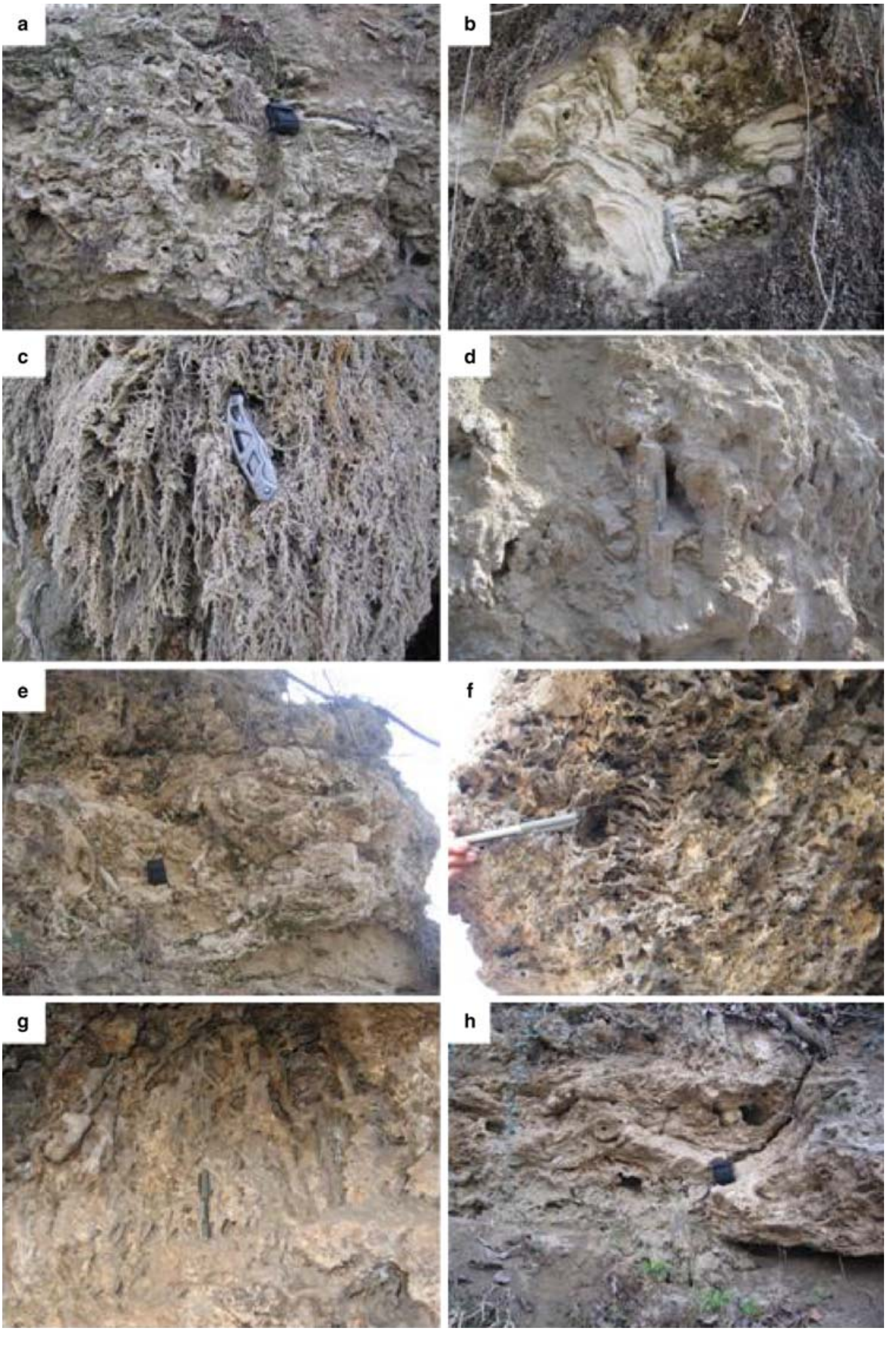

Fig. 5. Field views of different tufa components at the Güney perched springline tufa site. (**a**) Encrusted algal mass associated with macrophyte pieces was enclosed by fine grained detrital tufa layer (upper right corner); (**b**) The light-coloured and laminated tufa facies, lower slope, roadside section; (**c**) Calcified, fragile bryophyte cluster in the

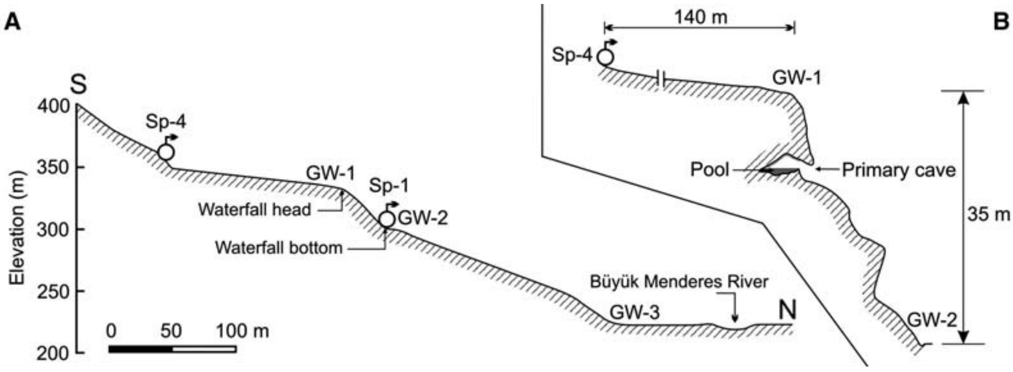

Fig. 6. A topographic cross section from the Sp-4 to the Büyük Menderes river valley in north–south direction. Details of the waterfall area between GW-1 and GW-2 were shown at the upper right. Sp-1 and Sp-4 are spring numbers, GW-1, GW-2 and GW-3 are *in-situ* measurement points at waterfall head (= splash zone), waterfall bottom and the lowermost slope, respectively.

were carried out on 11 recent and old tufa samples from different positions. Analyses were performed at the XRAL Laboratories in Ontario, Canada, by ICP-AAS. The isotope analyses of ^{14}C activity were made at Rudjer Boskovic Institute, in Radiocarbon and Tritium Laboratory, Zagreb, Croatia. The ^{14}C measurement was performed by liquid scintillation counter (LSC), Quantulus 1220 using two methods of sample preparation, a benzene synthesis method (LSC-B) and a CO_2 absorption method (LSC-D) (Horvatinčić *et al.* 2004). Mass spectrometry measurements of stable isotopes content, $\delta^{13}C$ and $\delta^{18}O$ were performed using a Finnigan Delta XP mass spectrometer at Joanneum Research Institute of Water Resources Management Hydrogeology and Geophysics Stable Isotope Laboratory, Graz, Austria. $\delta^{13}C$ and $\delta^{18}O$ in carbonates is expressed in ‰ deviations from the international standard PDB.

Depositional features of the perched springline tufa deposits

Perched springline tufas show distinct depositional morphologies in hilly country. The deposits are fan-shaped in plan and wedge-like in profile (Chafetz & Folk 1984; Pedley 1990; Ford & Pedley 1996; Carthew *et al.* 2003; Pedley *et al.* 2003). In the study area, the perched springline tufa site has been mainly divided into lobe-top terrace, waterfall (cascade) and lower slope zones.

Lobe-top terrace area

At the study site, there are two distinct lobe-top terraces developed in different elevations. One formed in front of Sp-2 whereas the other one formed in front of Sp-4 (Fig. 1c). The horizontal terraces are relatively narrow, long and restricted in areal extent. An elevated channel was developed on the lobe-top terrace (Fig. 3). This kind of channel previously was named as self-built channel (Bean 1971; Altunel & Hancock 1993; Özkul *et al.* 2002), catwalk/suspended channel (Violante *et al.* 1994; Pedley *et al.* 2003; Pedley 2009) at travertine and tufa sites. The water from Sp-4 flows along this gently sinuous channel for about 140 m across the subhorizontal terrace area before reaching the active waterfall head area or spill over point (GW-1 in Fig. 6). The channel was raised up from a few decimetres to metre scale above the pedestal of the lobe-top area. Lower half of the channel length is more elevated. Local people use both terraces for agricultural purposes.

Waterfall zone

In the study site, the waterfall area is located in the upper part of the system. The active cascade area is fed by the waters of Sp-4 and immediately SW of the active side is extinct presently (Fig. 4b). Another extinct cascade was developed in front of Sp-2 to the NE of the tufa site (Fig. 1c). The steep face of the waterfall is *c.* 35 m high and covered

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Fig. 5. (*Continued*) base of waterfall front; (**d**) Cylindrical macrophyte pieces in vertical position embedded in tufa body, lower slope, roadside section; (**e**) Fine- grained detrital tufas in the middle and lower right, distal slope on the roadside section; (**f**) Calcified bryophytes and coated stems; (**g**) Phytoherm framestone facies, immediately above the roadside section, lower slope; (**h**) Coated stems and micritic tufa crust underlain by detrital tufa. Scales: Camera cover is 13 cm, pen is 14 cm and pocket-knife is 5.5 cm.

mostly by the bryophytes (Fig. 4a, c, d). The bryophytes and other organic entities, which are in growth position, are main components of the phytoherm framestone facies (Fig. 4c, d). The exposed surface is green whereas the inner parts of the tufa are yellow because of the calcite cement that coats the surfaces.

There is an overhang on the uppermost part of the waterfall face (Fig. 4a, c) from which blocks of variable sizes commonly detach and fall to the foot of the waterfall. Blocks fell and a fracture was created in the overhang when the Buldan earthquakes of 5.2–5.6 magnitude occured close the Buldan town between 23 and 26 July in 2005 (Kumsar *et al.* 2008, p. 95–98).

The springline tufa body contains numerous primary cavities up to cave size in some cases. There are two main caves in the tufa site (Fig. 1c). One of them is under the splash zone within the active waterfall area (Fig. 3). A pool at the cave bottom is about 10 m wide and filled by percolating and drip waters (Fig. 4f). The second cave, to the NE, is located in the inactive tufa body that is close to Sp-2 (Fig. 1c). The pool in the bottom of this cave has been partly filled by wet lime mud and tufa fragments. Both caves have been partly or completely coated by various speleothems (Fig. 4f).

Lower slope area

The lower slope (or distal slope) lies below the foot of the waterfall where the slope gradient changes abruptly. In plan view, the lower slope tufas are fan-like and cover a broad area in comparison with the waterfall. The most of these deposits are composed of intraclast tufa. The lower slope deposits were exposed clearly along a road cuts approaching from the Cindere dam to the south–southwest and river bad (Fig. 4e). At the road cut surfaces, the lower slope deposits are consist of dominantly detrital tufas (Fig. 5a, e, h) and associated laminated tufa in some places (Fig. 5b) and macrophyte fragments eroded from the cascade area (Fig. 5d, e, h). The detrital tufa deposits have changed from silt to block in size. The light-coloured laminated tufa facies is composed of bryophyte layers and they should have been precipitated along flow paths on the slope (Fig. 5b). The macrophytes (= phytoherm framestone facies) in some cases are *in-situ* life position on the lower slope (Fig. 5g).

Age relationships of the coalescent tufa lobes

Perched springline tufas typically develop from single or multi-spring resurgences emerging on hill slopes. Subsequent valley incision may remove evidence of earlier deposits, although some sites as in the Tajuna valley (central Spain) demonstrate considerable preservation potential. As the river incises into its valley, there is often a corresponding reduction in the elevation of springlines along the valley size. There is, therefore, the possibility that deposits high on the upper valley sides are older than those lower down the slopes. In the case of multi-spring resurgences, age relationships between individual tufa mounds are more complex (Pedley *et al.* 2003).

At the Güney perched springline tufa site, tufa lobes at different levels have coalesced each others. There are inactive lobes at various elevations above and below of the active waterfall area. Therefore, a regular downslope decrease in ages of the tufa lobes was not expected. The preliminary ^{14}C dating of the some extinct tufa samples taken randomly gave ^{14}C age in the range from 2000 yr BP to 5800 yr BP (Table 2). The ^{14}C results are not corrected for the initial ^{14}C activity (A_o) of the carbonate (the 'reservoir' effect). According to the ^{14}C age data, extinct tufas are not older than Holocene (Horvatinčić *et al.* 2005). Further age dating is required before the precise ages of deposition can be determined.

Spring water physiochemistry

There are four main springs (Fig. 1c) and many smaller seeps in the Güney tufa site. The total flow rate of the springs is about 80 L/s. The discharge elevations are more or less the same for two springs (Sp-2 at 415 m and Sp-3 at 417 m a.s.l.; see Fig. 1c for spring location), whereas the other two discharge at lower elevations (Sp-1 at 320 m and Sp-4 at 355 m a.s.l.). The waters of Sp-2, Sp-3, and Sp-4 emerge from the boundary between the tufa deposit and schist – marble alternation forming aquifer rocks. The spring water of Sp-4 reaches the active waterfall area via a 140 m long channel. *In-situ* measurements show that the water physiochemistry of springs Sp-2, Sp-3 and Sp-4 are similar and that there are not distinct seasonal variations.

Hydrochemical features of the tufa precipitating waters are summarized in Table 1. The main spring waters discharge at 18.7–18.8 °C (Table 1) throughout the year. The water temperature of Sp-1 is lower (15.9 °C in winter to 16.7 °C in summer) than the others. The water temperature in the splash zone of the waterfall lobe-top area shows a regular variation that is linked to seasonal air temperatures. The seasonal fluctuations in the water temperature are about 0.5 °C in January and November while 0.2–0.5 °C in April and July. The biggest variation in water temperature occurs in the waterfall area due to water falling. The water temperature at the cascade bottom was decreased 0.5 °C in summer, 2.1 °C in

Table 1. *Chemistry of spring water at the Güney perched springline tufa site*

Date	No	T °C	EC	pH	CO_2	Ca	Mg	Na	K	Cl	SO_4	HCO_3	DIC	SIC	log pCO_2	Mg/Ca
October 2004	Sp-1	16.7	551	7.2	71	81.0	12.7	4.9	1.7	4.8	5.8	291	66.8	0.00	−1.74	0.26
	Sp-2	18.7	479	7.3	48	64.2	11.0	1.9	0.8	3.9	1.6	236	52.2	−0.02	−1.94	0.29
	Sp-3	18.7	482	7.4	44	65.2	10.4	1.9	0.8	3.9	2.0	232	50.6	0.04	−2.01	0.27
	Sp-4	18.8	477	7.3	43	64.0	10.8	1.8	0.8	3.9	0.6	236	51.8	0.01	−1.97	0.28
	GW-1	18.8	474	7.9	32	61.0	10.6	1.8	0.8	4.2	1.2	225	45.9	0.51	−2.54	0.29
	GW-2	17.2	391	8.2	24	47.0	7.8	1.9	0.8	4.3	0.6	178	35.83	0.59	−2.95	0.28
January 2005	Sp-4	18.7	482	7.2	65	64.8	9.8	1.8	0.8	4.0	2.0	243	54.7	−0.07	−1.86	0.25
	GW-1	18.3	475	7.7	56	62.4	9.7	1.8	0.8	4.1	2.0	222	45.9	0.35	−2.38	0.26
	GW-2	13.5	392	8.1	38	45.2	9.3	1.8	0.8	4.1	1.6	182	36.7	0.47	−2.91	0.34
	GW-3	13.2	376	8.3	6	35.6	9.2	1.8	0.8	4.2	2.6	152	30.6	0.44	−3.13	0.43
April 2005	Sp-4	18.7	481	7.3	53	63.7	10.1	1.7	0.8	4.3	1.8	240	53.0	−0.01	−1.94	0.26
	GW-1	18.9	472	7.7	38	58.9	9.8	1.8	0.8	4.2	1.8	216	44.6	0.32	−2.39	0.28
	GW-2	16.8	400	8.1	26	51.1	9.2	1.8	0.8	4.2	1.9	188	38.0	0.52	−2.81	0.30
	GW-3	16.9	381	8.3	5	35.2	9.1	1.9	0.8	4.5	2.2	149	29.9	0.51	−3.15	0.43
July 2005	Sp-4	18.8	482	7.4	40	63.8	10.7	1.8	0.8	3.9	2.1	234	51.2	0.02	−1.99	0.28
	GW-1	19.3	470	8.0	31	60.7	10.4	1.8	0.8	4.0	1.9	222	45.1	0.58	−2.62	0.29
	GW-2	18.8	408	8.2	23	48.1	8.2	1.8	0.8	3.9	2.0	182	36.7	0.60	−2.91	0.28
	GW-3	21	356	8.3	4	46.3	8.1	1.8	0.8	4.1	2.2	171	34.4	0.71	−3.05	0.29
November 2005	Sp-4	18.7	486	7.4	31	62.6	10.5	1.8	0.8	4.0	1.1	229	49.5	0.06	−2.06	0.28
	GW-1	18.2	478	8.0	25	58.2	10.3	1.8	0.8	4.1	1.2	221	44.7	0.62	−2.70	0.30
	GW-2	13.6	421	8.3	19	45.1	8.9	1.7	0.8	4.1	1.1	178	35.8	0.61	−3.07	0.33
	GW-3	14.1	385	8.5	3	32.8	8.2	1.8	0.8	4.0	1.4	137	27.5	0.58	−3.39	0.42

SIC, calcite saturation index; EC (electrical conductivity), μS/cm; pH, standard unit; DIC (dissolved inorganic carbon), ppmC; log pCO_2, atm.; Mg/Ca, molar ratio; other constituents are in ppm.

Table 2. *Major, trace element and isotope compositions of the Güney perched springline tufa deposits*

Sample no*	Si	Al	Fe	Mg	Ca	Ba	Sr	$MgCO_3$	^{14}C measurement			$\delta^{13}C$	$\delta^{18}O$
									Method	pMC	yr BP	(‰ PDB)	
1	2150	580	980	1860	383500	97	236	0.80	B49	63.8 ± 0.5	3610 ± 60	−9.13	−8.44
									D172	60.5 ± 2.0	4030 ± 270		
2	9380	4230	2800	3120	341400	108	222	1.50	B56	64.1 ± 0.6	3565 ± 70	−7.71	−8.16
									D193	68.5 ± 2.0	3040 ± 230		
3	140	50	700	3180	379200	152	249	1.38	B51	65.7 ± 0.5	3375 ± 60	−7.69	−7.90
4	2000	890	840	3240	368000	125	230	1.45	B52	65.5 ± 0.5	3395 ± 60	−7.85	−8.10
									D182	65.4 ± 1.9	3415 ± 230		
5	930	420	490	2220	380900	143	225	0.96	B68	76.0 ± 0.4	2200 ± 45	−6.25	−8.14
6	1910	370	1050	5940	377300	136	237	2.56	B57	73.6 ± 0.6	2463 ± 70	−6.00	−7.40
									D190	77.9 ± 2.1	2010 ± 220		
7	1440	580	770	3300	378300	33	262	1.43	D228	68.0 ± 2.1	3096 ± 245	−7.99	−7.59
8	8770	2060	1680	7440	352200	183	285	3.40	D225	62.7 ± 1.9	3748 ± 249	−8.36	−8.11
9	190	160	770	1380	388900	192	322	0.59	B59	48.6 ± 0.5	5790 ± 80	−7.69	−8.12
									D200	50.5 ± 1.4	5490 ± 220		
10	6910	1790	1960	2220	375800	150	222	0.97	B61	65.0 ± 0.6	3460 ± 70	−8.19	−8.03
									D202	67.0 ± 1.6	3220 ± 190		
11	980	320	490	1680	381700	138	253	0.73	D248	67.9 ± 1.8	3108 ± 215	−6.53	−7.65
12									B55	70.6 ± 0.6	2800 ± 70	−6.93	−7.88
Average	3164	1041	1139	3235	373382	133	249	1.43				−7.52	−7.96

*The samples 1, 3, 4 and 12 are recent tufas. Elements are in ppm, $MgCO_3$ values (in mol%) were calculated from Mg and Ca data assuming these are the only cations in the carbonate fraction. ^{14}C activity was determined with LSC method with 2 sample preparation procedures (B- benzene synthesis and D- CO_2 absorption method). ^{14}C results were expressed as ^{14}C activity in percent of modern carbon (pMC) and as ^{14}C age in yr BP (not corrected for the initial ^{14}C activity Ao).

spring, 1.6–4.6 °C in autumn and 4.8 °C in winter with respect to the splash zone. These variations in water temperature are dependent on seasonal air temperature. In the city centre of Denizli according to long-term meteorological data, average air temperatures are 5.9 °C in January, 14.5 °C in April, 27.5 °C in July and 11 °C in November.

The pH value increases in downflow direction, from 7.2–7.4 at the spring orifice (measurements at Sp-4), to 7.7 at waterfall head (point GW-1 in Fig. 6), and to 8.0 at the waterfall bottom (point GW-2) as a result of CO_2-degassing. The biggest pH variation has occured during the flow from top to bottom (7.7–8.1) of the waterfall in winter season (Table 1). Similarly, the HCO_3 value also decreases rapidly downflow, from Sp-4 to GW-3 (see Fig. 6).

The CO_2 value in the water of Sp-4 is higher (53–65 ppm) in winter and spring seasons. It is lower (6–15 ppm) in summer and autumn seasons. Maximum CO_2 – degassing from the water occured in January. The calcium content of the Sp-4 was almost constant with 64 ppm in five sampling period. The Ca values decrease sharply in the splash zone. The Mg ratio ranged from 7.8–12.7 (Table 1). Mg/Ca molar ratios of the Sp-4 are lower in wet season compared with dry period because of dilution. According to hydrochemical analysis, the dominant ions in the spring waters are calcium and bicarbonate (Table 1) and consequently, all spring waters in the tufa site are type of $Ca–HCO_3$.

The calcite saturation indices (SIC) in the spring orifice are within borderline scale potential (−0.02–0.06); however, they increase rapidly along the flow path because of CO_2-degassing and the waters are supersaturated with respect to calcite at splash zone of the waterfall (Table 1). These values reach up to 0.6 at the waterfall bottom. The SIC values are highest in the summer season and lowest during the winter. Similarly, the pCO_2 and DIC values of the spring water change naturally like the SIC values. The CO_2 partial pressure of the water in GW-3 location is close to the atmospheric pressure.

The tritium value of the spring Sp-1 and Sp-4 is 5.9 TU. These isotopic data indicate that the spring waters are of meteoric origin and ascend to the surface following shallow circulation. The $\delta^{13}C$ in dissolved inorganic carbon (DIC) of the Sp-4 is −3.71‰, indicating that the inorganic carbon was derived mainly by dissolution of marine carbonate.

Mineralogical, chemical and biological composition of the tufa deposits

Mineralogical composition

Tufa samples are mainly composed of calcite (Fig. 7) with minor amound of quartz and feldspar. The calcite is mostly micrite and microspar (5–20 μ) in size. The microspar calcite occurred as cement readily distinguishable from the micritic groundmass, and commonly fills pores (Fig. 7e–g). Micropores on some of the crystal surfaces are possibly from dissolution of inclusions (perhaps loss of organic fragments) (Fig. 7h). The quartz grains, which are scattered throughout the micritic ground and commonly single quartz grains in silt size, probably derived from the schists around the tufa site.

Biological composition

Apart from hydrophytic macrophytes, the tufa deposits also include bryophytes, cyanobacterial filaments, and diatoms. Bryophytes dominate in the waterfall area. The diatom frustules were determined as species *Cymbella* sp. and *Synedra* sp. (Figs 7b & 8e, f–h). In some cases, pulmonate gastropods were observed occasionally within the fine grained detrital tufa of the lower slope deposits.

Chemical composition

The eleven recent and old tufa samples were taken from different parts of the site. The results of major and trace element analyses of the samples were given in Table 2. The Mg content ranged from 1380–7440 with an average of 3235 ppm. The $MgCO_3$ of the tufa deposits ranges from 0.59–3.40 mol% with an average of 1.43 mol%. According to these values, the calcite in the tufa is clearly low magnesian calcite. The Mg contents of the tufa samples are more or less similar with the Urrea de Jalõn tufa deposit, Ebro basin, NE Spain (Arenas *et al.* 2000), whereas the higher values were reported from some travertine occurances in hiydrothermal origin (Minissale *et al.* 2002). Ba and Sr compositions of the tufa samples are 33–192 ppm and 222–322 ppm, respectively. The Ba and Sr contents are similar or slightly higher than those in fluvio-lacustrine tufas in the central Ebro Depression, NE Spain (Arenas *et al.* 2000), while Ba content in Quaternary tufa stromatolite from central Greece is also in similar value (Andrews & Brasier 2005).

Radiocarbon and stable-isotope composition

Preliminary results of ^{14}C and stable-isotope ($\delta^{13}C$ and $\delta^{18}O$) composition of these tufa deposits were reported in Horvatinčić *et al.* (2005). The ^{14}C activity of recent tufa samples in the Güney springline tufa site are 60–70% of modern carbon (pMC) (Table 2, sample 1, 3, 4 and 12). This A_o value is

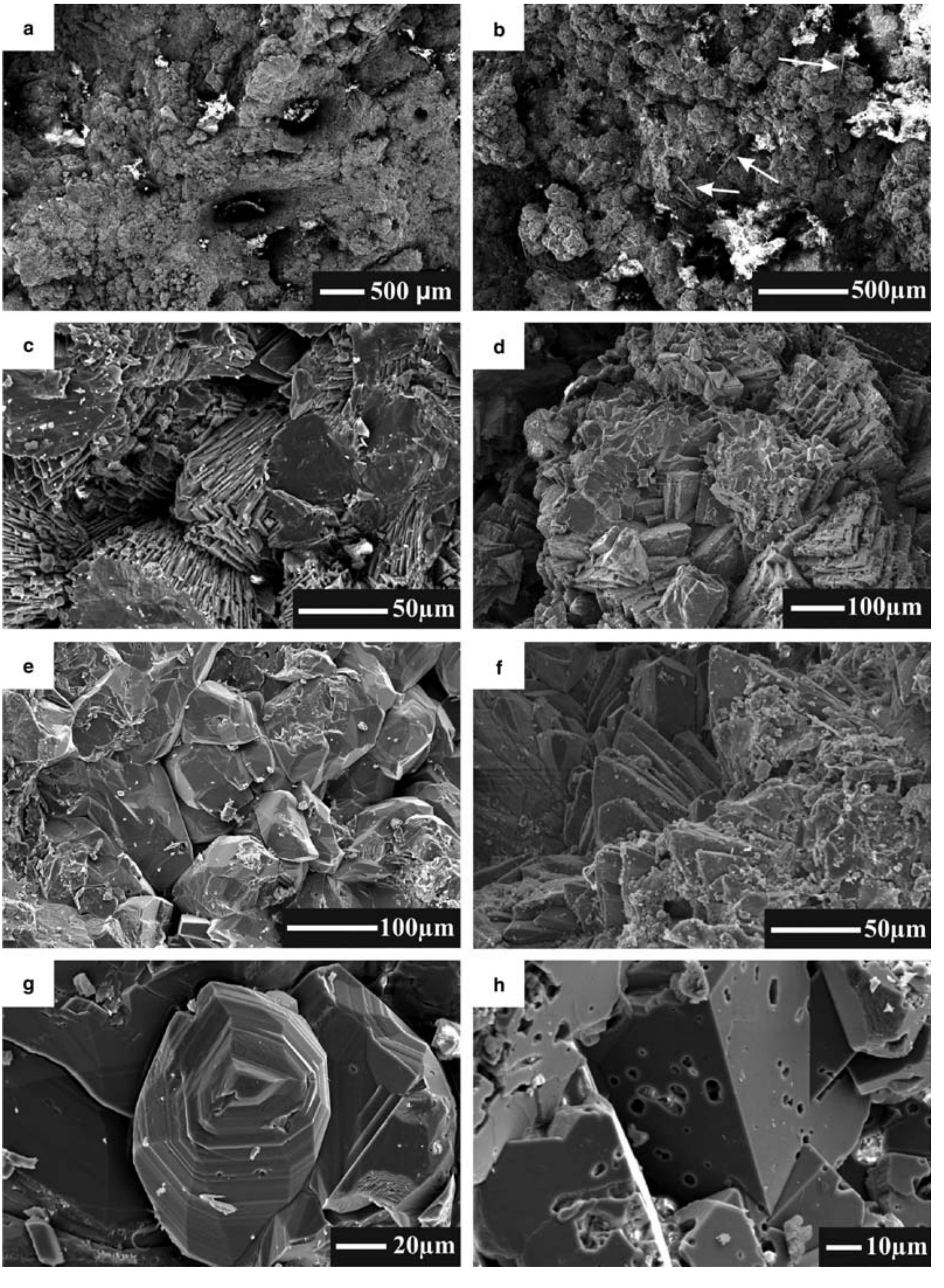

Fig. 7. SEM images of mineral precipitates from the Güney perched springline tufa site. (**a**) Surface of rough and porous tufa deposits; (**b**) Tufa deposits in (a) associated with rod like microbial components (arrowed); (**c**) Bundles of calcite crystals with blade and spearhead form; (**d**) Euhedral microcrystalline calcite; (**e**) Calcite rhombs; (**f**) Secondary calcite crystals in blade shape developed in a pore; (**g**) Close view of calcite rhombs in (e); (**h**) Calcite crystals with smooth surfaces and micropores.

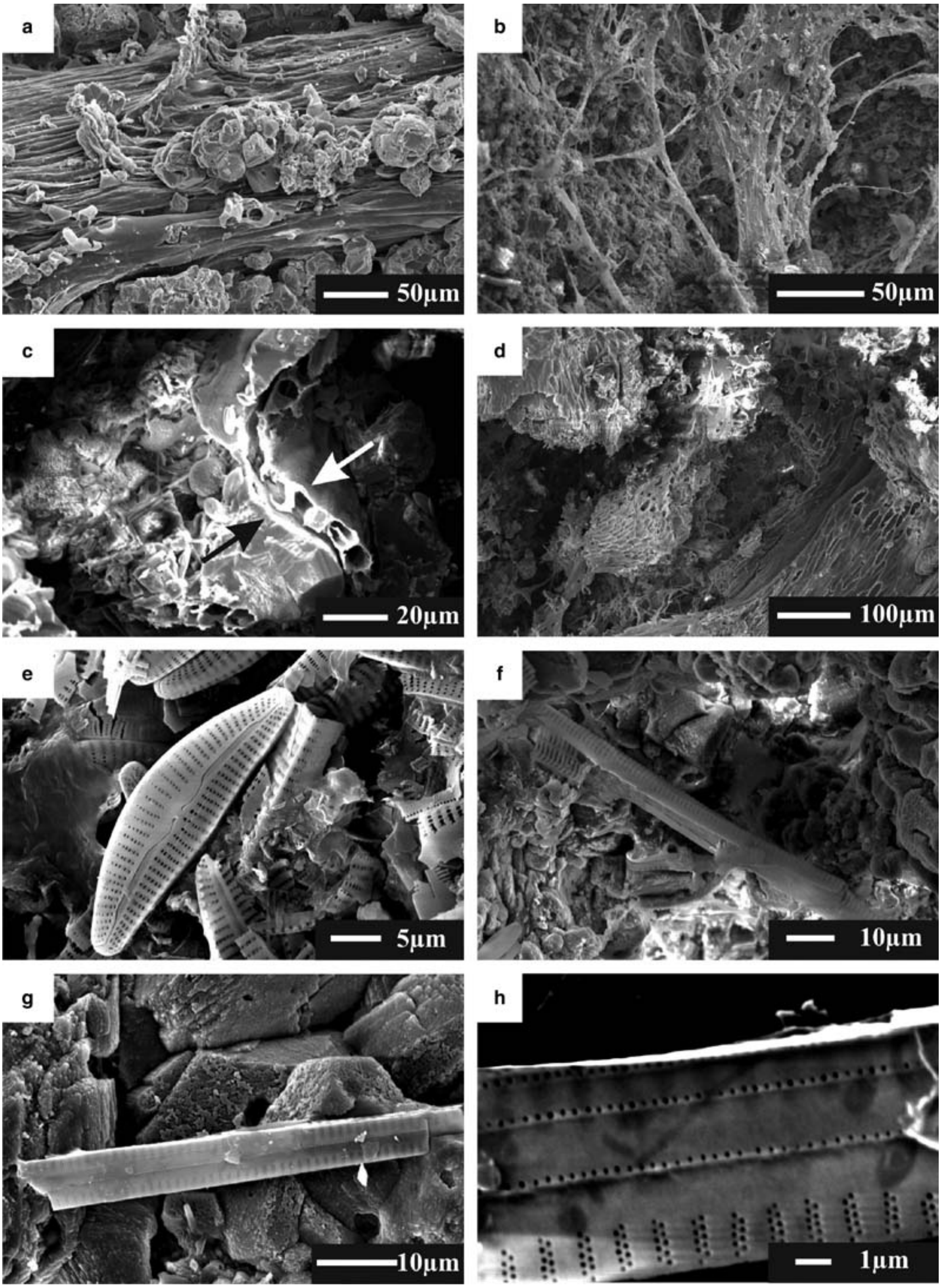

Fig. 8. SEM images of microbial components from the tufa deposits. (**a**) Longitudinal, fibrous microbial component and adhered calcite crystals on its surface; (**b**) A network of microbial filaments and calcified extracellular polymeric substances (EPS); (**c**) Curved leaf (between arrows) and diatoms in the middle; (**d**) Longitudinal cellular bryophyte tubes; (**e**) Lenticular diatom frustules (*Cymbella* sp.), some diatoms deformed and broken; (**f**) Rod-like diatom, *Synedra* sp.; (**g**) *Synedra* sp. attached on calcite rhombs; (**h**) A close view of the diatom *Synedra* sp. in (g).

typical for carbonates precipitated from the fresh water system where ^{14}C activity of dissolved inorganic carbon (DIC) is result of mixture of biogenic/atmospheric CO_2 and dissolved mineral carbonates, for example, limestone. The $\delta^{13}C$ and $\delta^{18}O$ values of active and passive tufa samples are in the range from −9.13 to −6.0‰, and from −8.44 to −7.40‰, respectively (Table 2). More negative $\delta^{13}C$ values of the Güney site indicate that most of the ^{14}C is of atmospheric CO_2 and/or biogenic origin.

Discussion

The prominent features of the studied site were compared with some well-known tufa sites throughout Europe in Table 3.

The Güney waterfall site is composed of coalescent tufa bodies and includes an active waterfall area. The two distinct lobe-top terrace areas took place above the active waterfall. Horizontal–subhorizontal lobe-top area is an indication of mature stage of perched springline tufa deposits (Pedley 1990; Ford & Pedley 1996; Pedley *et al.* 2003). Consequently, some of the tufa lobes have reached a mature stage. In the study area, the flat terraces possibly developed in consequence of prograding lobe fronts and issue of antecedent topography. A self-built channel has been developed at one of the lobe-top terraces. This kind of channels was observed at thermal areas in Pamukkale and surroundings in the Denizli basin, western Turkey (Bean 1971; Altunel & Hancock 1993; Özkul *et al.* 2002). Similar channels have been mentioned from another perched springline tufa site (i.e. Rochetta a Volturno, Italy; Violante *et al.* 1994), but not seen in the Spanish examples (Pedley *et al.* 2003).

The inactive Holocene tufa samples are from 2000–5800 yr BP old, based on the ^{14}C dating method (Horvatinčić *et al.* 2005). Age relationships between coalescent tufa bodies in perched springline sites are quite complex (Martín-Algarra *et al.* 2003; Pedley *et al.* 2003). In the study area, the present multi-spring resurgences and individual tufa lobes coalesced occur at various elevations. Thus, a regular downslope trend in ages is not expected. One of the reasons of this situation may be heterogenity within the aquifer rocks. Earthquake activity in the region (Kumsar *et al.* 2008, p. 95–98) may have been changed the settings of the spring resurgences through time. In some Spanish sites, regular trends have been recorded in downslope directions. Gonzáles Martín *et al.* (1989), for example, indicated that the higest deposits at Tajuña sites, NE of Madrid, are no longer active, whereas those in the valley bottom are still developing. This suggests a decrease in age of individual mounds in a downslope direction. This is not always the case, hovever, as new tufa lobes can develop above older sites of deposition (Pedley *et al.* 2003). Furthermore, Martín-Algarra *et al.* (2003) pointed out that well-defined tufa steps in Granada basin (south Spain) were deposited by springs that migrated downslope in time.

Tufa-depositing spring waters have distinct chemical compositions. Most waters emerging from karstic massifs commonly are of $Ca–HCO_3$ and $Ca–HCO_3–SO_4$ types and supersaturated with respect to calcite (Andreo *et al.* 1999; Horvatinčić *et al.* 2005). In some areas, however, the chemical compositions of karstic waters may be slightly different as in the Honaz site, Denizli, Turkey (Horvatinčić *et al.* 2005). In addition, Pentecost (2000) assumed that the Matlock Bath deposit and associated spring waters, Derbyshire, UK were 'thermogene travertine' and 'thermal water', respectively, depending on chemical compositions. The Matlock Bath waters are really deep-cycled meteoric waters, which are only a few degrees above ambient temperature (pers. comm., Pedley 2009). The Matlock Bath site is a good example of a perched springline tufa model in aspect of its formation and morphology and fits his classification (Pedley 1990) very well.

At the Güney site, the hydrochemical parameters of the tufa-precipitating waters were monitored seasonally for more than one year (Table 1). Downflow, the pH, SIC, Mg/Ca values increased whereas the CO_2, EC, Ca, Mg, HCO_3, and DIC decreased. The Na, K, Cl and SO_4 values did not change during the study period. The DIC concentrations were higher in January (winter season) and lower in November such as in the recent freshwater carbonates of River Krka, Croatia (Lojen *et al.* 2004).

Apart from the Güney site, there are two other tufa sites in the Denizli basin, one at Sakızcılar and the other at Honaz. The tufa deposits and spring waters of Güney and Sakızcılar sites show similar characteristics in water chemistry. In contrast, the water and tufa chemistry at the Honaz site, which is located along a normal fault zone (Bozkuş *et al.* 2000), is different. The water temperature, electrical conductivity, dissolved anion and cation values of the Honaz site are higher than the other two tufa sites because of longer residence time. Waterfall tufa area is one of the most important components of perched springline and fluvial models as investigated in some European sites previously. Also this area takes place in front of tufa barrage downstream in a fluvial model and passes into lake deposits upstream. The most rapid tufa precipitation occurs in waterfall front of a perched springline tufa site (Pedley *et al.* 1996; Pentecost 2000; Pedley *et al.* 2003; Carthew *et al.* 2003; Andrews 2006; Pedley 2009).

Table 3. *Comparative features of some European perched springline tufa sites well-documented*

	Pentecost 2000; Pedley *et al*. 2003 Matlock Bath, Derbyshire, UK	Violanta *et al.* 1994, Rochetta a Volturno, central Italy	Pedley *et al.* 2003, Rio Tajuña valley, central Spain	Martin-Algarra *et al.* 2003, Granada basin, central Spain	This study, Güney Şelalesi, Denizli, SW Turkey
Climate	Temperate Rainfall 1000 mm pa*	Semi-arid	Semi-arid Rainfall <490 mm pa*	Semi-arid Rainfall <490 mm pa*	Semi-arid Rainfall 548 mm pa, ann mean air temp. 13.5 °C
Altitude	100–130 m	450–550 m	750–800 m	950–1120 m	200–500 m
Spring	Multi-spring resurgences, water temp. close to 20 °C Ca-Mg-HCO_3 type waters	Ambient temperature or low thermal waters	Multi-spring resurgences	Multi-spring resurgences, migrating springs downslope in time	Multi-spring resurgences, spring water temp. = 18.7 °C, Ca–Mg–HCO_3 type water
Morphology	Western lower slope of the River Derwent with a few cascades	Lobe-shaped configirations and minor terraces are visible	Mature deposits are characterized by lenticular to wedge-shaped, downslope-facing lobate profiles	Four well-defined steps succeeding each other in downslope direction	Lobate or fan-shaped mounds in plan, lenticular, wedge-shaped in profile, flat top (mature stage)
Lob top surface	Suspended channels	Terraced, flat upper surface associated with suspended channel (catwalk) and very shallow lakes	Gently convex or flat upper surface in mature stage. Organic-rich and oncoidal deposits	Flat upper surface, Abundant oncoid up to gravel size	Flat upper surface (maturity stage) associated with suspended channel, stand of trees, used as agricultural area
Areal extent	6 hectars	1500 hectars	From a few square metres up to hundreds of hectars	150 hectars (1.5 km^2)	20 hectars
Primary cavities	Present	Large cavities and several caves, speleothem-lined cave walls	Abundant, speleothem-lined	Decimeter to meter-size voids partially speleothem-lined	Abundant cavities up to cave size with speleothem-lined
Stromotolite		Stromotolites encrusring travertine intraclasts	Flat-topped stromotolite heads below bryophyte curtain	Thin, planar to undulose stromotolite crust	Thin, undulose stromotolite crust
Flora	Bryophyte (moss), diatom, mollusca, ostracoda, pollen	Moss (bryophyte), cyanobacteria	Moss (mainly bryophyte), some grasses and trees	Decimeter-sized moss mound, patches of canes, leaves of *Salix* sp., *Quercus* sp., and herbaceous veget.	Some grasses and trees, moss (mainly bryophyte), diatom
Fauna			Pulmonate gastropods usually dominant in distal slope facies by	Gastropod	Gastropod
Tufa breccia, palaeosol		Filled up erosional channels with intraclasts on upper slope associated with palaeosols	Detrital tufas associated with palaeosols	Common as calcified plant detritus on distal slope	Common on distal slopes and interlobe areas
Age relationship			No regular age trend downslope	Tufa steps get younger downslope with time	No regular age trend downslope

*Rainfall data taken from Viles *et al.* 2007.

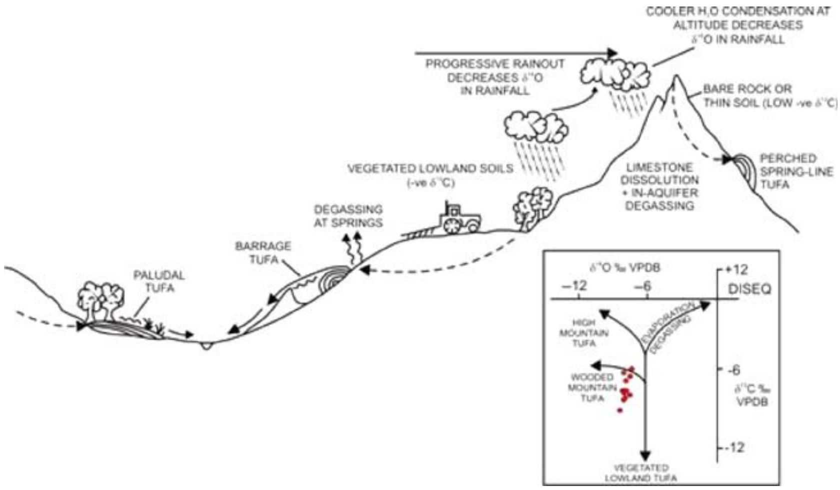

Fig. 9. Regional setting of the Güney springline tufa deposits base on the $\delta^{18}O$ and $\delta^{13}C$ stable isotope data plotted on figure 3 of Andrews (2006). The tufa deposits in this study correspond to 'wooded mountain tufa'. See for details Andrews (2006).

Stable isotope signatures in tufas have useful environmental and climatic information (Andrews *et al.* 1997). Based on stable isotope distribution (Fig. 9), the Güney springline tufa deposits, which are located below 500 m in altitude, correspond to the 'wooded mountain tufa' of Andrews (2006). In the same time, the distribution of stable isotope data of the tufa deposits show similarity with Dinaric

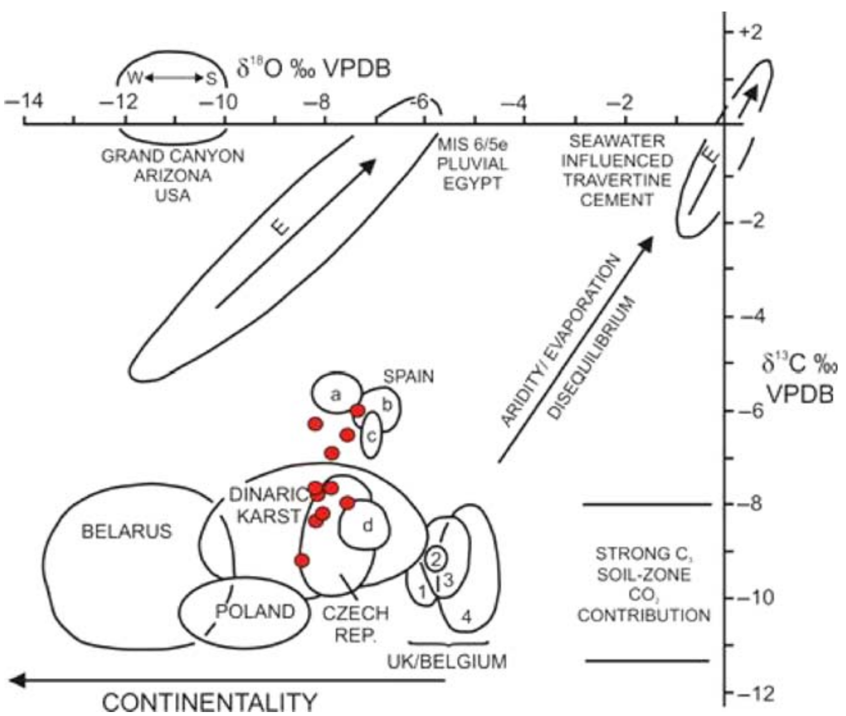

Fig. 10. Continental setting of stable isotope data of the Güney perched springline tufa deposits plotted on Figure 7 of Andrews (2006). The stable isotopes ($\delta^{18}O$ and $\delta^{13}C$) plotting of the tufas show similarity with Dinaric karst, Czech Republic and Spanish precipitates in European scale.

karst (Horvatinčić *et al.* 2003), Czech Republic and Spanish precipitates in European scale (Fig. 10).

Conclusions

The Güney tufa site is a typical representative of perched springline tufa model in eastern Mediterranean. The site with lobe-top terraces partly reached in mature stage. Numerous cavities have developed behind of the tufa lobes; some of them reached more than 10 m in size. In the Güney site, tufa deposition began at least 5800 yr BP.

The tufa-precipitating waters supersaturated in calcite outflow from multi-spring points and are of $Ca-HCO_3$ in origin. According to hydrochemical and isotopic composition, the site waters are clearly meteoric and shallow circulated. Radiocarbon and stable-isotope composition of the tufa deposits support meteoric origin. Additionally, the stable-isotope values show similar distribution with south European countries.

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