The Ab Ask mineral springs are located 85 km northeast of Tehran, in the southern range of the Damavand volcano. Deposits of these calcareous springs are mainly precipitated as travertine. Petrographical, mineralogical, and stable isotope studies were conducted on different types of travertine to determine their genesis and factors that govern carbonate precipitation. Based on sedimentation consequence and lithofacies these travertines are categorized as first type (fresh travertine), second type (fissure–ridge, dam, and cascade), and third type (laminated) travertines, illustrating a specific condition of formation, deposition and diagenesis. Combined XRD and microscopic investigations show that the Ab Ask travertines are composed of about 95% calcite and a minor amount of quartz along with iron oxide impurities. The origin and transport of springs water from which travertine was precipitated are elucidated by $^{13}$C and $^{18}$O isotopic studies of the travertines. $\delta^{18}$O and $\delta^{13}$C values of travertines increase (from $-13.0$ to $-6.3‰$ VPDB and from $6$ to $9.8‰$ VPDB, respectively) with increasing distance from the spring orifice. This significant increase is attributed to temperature decrease, rapid degassing of CO$_2$, and biological activities. It seems that CO$_2$ content of these fluids may have originated from limestone decarbonation. Based on the integrated petrographic and stable isotope study, the Ab Ask travertines can be thermogenic in origin.

Key words: Ab Ask, Damavand, hot springs, stable isotope, travertine

Addresses: S. Rahmani Javanmard, F. Tutti, S. Omidian, M. Ranjbaran

*Corresponding authors' e-mail: tutti@khayam.ut.ac.ir

Received: October 4, 2012; accepted: December 25, 2012
Introduction

Travertine is a type of freshwater limestone deposited from cold or hot spring waters, or less commonly from percolating waters (Wyatt 1986). The term travertine is also commonly used in a broader sense to refer to all non-marine limestone formed under climatic controls in streams, lakes, springs, and caves (e.g. Sanders and Friedman 1967; Viles and Goudie 1990; Pentecost and Viles 1994), while tufa refer to limestone precipitated in cool or near-ambient temperature water and characterized by high micro- and macrophyte, bacteria, and invertebrate content (Ford and Pedley 1996). In general, travertine is composed of mainly calcite with low-Mg content, or less abundantly, of aragonite (Guo and Riding 1992; Fouke et al. 2000; Pentecost 2005). Physical processes such as agitation of the water or variations in flow related to functional karstification of aquifers (Martin 1988) and biological processes of certain microorganisms, such as algae and bacteria (Casanova 1986), can affect travertine precipitation and facies. Based on the origin of carbon dioxide, travertine can be divided into two classes (Pentecost and Viles 1994; Pentecost 2005). The kind which obtains CO₂ mainly from organic activity in the soil is named meteogene travertine while thermogene travertine acquires CO₂ from thermal processes, including magmatic degassing or decarbonation of limestone during thermometamorphic processes (Pentecost and Viles 1994; Ford and Pedley 1996; Minissale et al. 2002). Thermogene travertine is usually massive and contains less organic materials than meteogene travertine, and is essentially found in regions with recent volcanic or high tectonic activity. The worldwide distribution of travertine and its genesis from hot springs have been widely described by many investigators: in the Pannonian Basin by Schweitzer and Scheuer (1995) and Kele (2009), in the Yellowstone area by Chafet and Guidry (2003), in Turkey by Altunel and Hancock (1993a, b, 1994), in France by Pentecost (1991, 1995), in the Turkana Basin by Renaut et al. (2002), in the Colorado Plateau by Shipton et al. (2004), in Rapolano Terme (Italy) by Brogi and Capezzuoli (2009), in the Betic Cordillera by Martinez-Diaz and Hernandez-Enrile (2001), etc. A detailed stable isotope study on the Pamukkale travertine was carried out by Kele et al. (2011).

The principal purpose of this work is to carry out for the first time a detailed study on representative samples of the Ab Ask travertine in the vicinity of Damavand volcano, which is in turn a well-known volcano from a global tectonics and volcanic point of view. Petrography, combined with the C and O stable isotope studies, has been performed on this travertine in order to define the origin of CO₂ in the waters from which these carbonates were deposited. The present study could, to some extent, provide valuable information on the paleoenvironment of travertine precipitation and determine the local processes that influence carbonate lithology, as well as elucidate the relationship between the thermal springs and volcanic activities of Damavand through time.
Geologic settings

The Ab Ask travertine is located around the hot springs in a village of the same name southeast of Damavand volcano, northeast of Tehran (Fig. 1). The exposed geologic formations in the area were studied by many geologists (e.g. Allenbach 1966) and consist of Paleozoic and Mesozoic sediments, mainly limestone, shale and sandstone, as well as Tertiary-Quaternary rocks including pyroclastics, ash falls and lava flows (Fig. 1). This area is located in the middle of the Central Alborz, which is a tectonically very active zone in the Iranian Plateau. Recent and active tectonics in the Alborz mountain range has been studied by many geologists (e.g. Tchalenko 1974; Ambraseys and Melville 1982; Berberian 1983; Alavi 1996; Jackson et al. 2002).

The structural architecture of the Alborz remains controversial issue. Axen et al. (2001) noted that several of the thrusts have normal separations and interpreted the assemblage as an asymmetrical, south-vergent, transpressional flower structure. Similarly, Jackson et al. (2002) and Allen et al. (2003) considered the Alborz to be a sinistral transpressional belt, where slip is partitioned between sinistral strike-slip faults and thrust faults. Alavi (1996) interpreted the Alborz as a thin-skinned fold-and-thrust belt that has formed a complex composite antiformal stack, which is cut by detachment and normal faults that drop the south Caspian down relative to the Alborz. There are copious faulting and folding activities within it. To identify the major ranges of fractures and faults in studied region, Aster Remote Sensing satellite image studies were performed (Fig. 2). These studies showed that the best linear feature exposures are visible in the region of the 4,3,1 band combination in the RGB environment. Two linear trends, ESE (for major lineation) and ENE (for minor lineation, but more dispersion) were identified. Concentrations of these lineations in the Ab Ask region were attributed to the multiple fractures in this area. These fractures are assumed to be the cause of the formation of hot water springs and travertine deposition.

Descriptions of the Ab Ask springs

Temperature, pH, EC and TDS data of the four hot springs are summarized in Table 1 (Shemshaki et al. 2008). The hot springs of the Ab Ask area are slightly acidic (pH = 6–6.41) and have temperatures ranging between 23°C and 30°C, while EC varies from 1.39 to 3.65 mS cm⁻¹ and TDS ranges from 1.81 to 2.79 g/L. The EC values obtained for the Ab Ask springs (1.39–3.65 mS cm⁻¹) fall in the range of thermogene waters (1–10 mS cm⁻¹; see Pentecost 2005).

Sampling and methodology

Based on travertine morphology and external lithofacies, 50 rock samples were collected in order to determine their mineralogical properties, and texture; among them 16 samples were chosen for isotopic analyses. Thin section of rock
specimens were studied by polarized microscope and some selected samples were then analyzed by X-ray powder diffraction (XRD) with Cu $K_{\alpha1}$ radiation at the Solid State Research Laboratory (University of Damghan), using a Hitachi S-4160 Scanning Electron Microscope at the University of Tehran. The isotopic composition of the travertine was measured according to the method described in Allenbach and Shteiger (1966).

![Geologic map showing the position of travertine deposits of the Ab Ask hot springs.](image1)

**Fig. 1**

Existing lineations in Aster satellite image with the 4,3,1 band combination.

**Table 1**

Names and physical–chemical parameters of the Ab Ask Hot Springs

<table>
<thead>
<tr>
<th>Spring name</th>
<th>T (°C)</th>
<th>pH</th>
<th>EC (mS cm$^{-1}$)</th>
<th>T.D.S (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zaghe Spring</td>
<td>29</td>
<td>6.41</td>
<td>3.65</td>
<td>1.82</td>
</tr>
<tr>
<td>Ghay Bal Spring</td>
<td>23.4</td>
<td>6.28</td>
<td>1.39</td>
<td>2.79</td>
</tr>
<tr>
<td>Mokhaberate Spring</td>
<td>29.2</td>
<td>6.38</td>
<td>3.64</td>
<td>1.81</td>
</tr>
<tr>
<td>Yeyllagh Spring</td>
<td>30</td>
<td>6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
in detail in Breitenbach and Bernasconi (2011). Approximately 100 micrograms of powder were reacted with 100% phosphoric acid at 70°C in a Thermo Fisher Gas Bench device connected to a Thermo Fisher Delta V mass spectrometer at the ETH Stable Isotope Laboratory (Zurich, Switzerland). The reproducibility of the measurements based on replicated standards was ±0.05‰ for δ13C and ±0.06‰ for δ18O. The instrument is calibrated with the international standards NBS19 (δ13C = 1.95 and δ18O = −2.2‰) and NBS18 (δ13C = −5.01 and δ18O = −23.01‰). The isotope values are reported in the conventional delta notation with respect to VPDB (Vienna Pee Dee Belemnite). All analytical results are displayed in Table 3.

Results

Mineralogy and petrography

Microscope studies have shown that the studied travertine samples are mostly composed of calcite which was confirmed by the results of the powder X-ray diffraction technique (Table 2). Based on their sedimentation sequence and lithofacies, they can be divided into several groups and subgroups.

1.) First type travertine (stream channel deposits). These loose and porous deposits constitute nodular forms and thin layers with greenish surfaces (Fig. 3A). Their nodular shape may result from colonization by algae, especially cyanobacteria (Pentecost 2005). Microscopic studies show that they are composed of lublinite-like (acicular) crystals (Fig. 3B). The origin of these crystals could be associated with the late stages of cement formation (Gruszczynski et al. 2004). Lublinite-like crystals may have formed as a felt during evaporation when the bacterial-mat pond had been dried out (Folk et al. 1985). These crystals tend
Table 2
Result of XRD analyses of travertine and veins from the Ab Ask area

<table>
<thead>
<tr>
<th></th>
<th>SR T1</th>
<th></th>
<th>SR A22</th>
<th></th>
<th>SR B32</th>
<th></th>
<th>SR A40</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>d-value</td>
<td>Intensity %</td>
<td>h k l Minerals</td>
<td>d-value</td>
<td>Intensity %</td>
<td>h k l Minerals</td>
<td>d-value</td>
<td>Intensity %</td>
<td>h k l Minerals</td>
</tr>
<tr>
<td>3.821</td>
<td>18</td>
<td>1 0 2 Ca</td>
<td>3.836</td>
<td>5.7</td>
<td>1 0 2 Ca</td>
<td>3.824</td>
<td>4.9</td>
<td>1 0 2 Ca</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.348</td>
<td>1.7</td>
<td>1 0 1 Q</td>
<td>3.339</td>
<td>2.5</td>
<td>1 0 1 Q</td>
</tr>
<tr>
<td>3.622</td>
<td>100</td>
<td>1 0 4 Ca</td>
<td>3.024</td>
<td>100</td>
<td>1 0 4 Ca</td>
<td>3.016</td>
<td>100</td>
<td>1 0 4 Ca</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.016</td>
<td>100</td>
<td>1 0 4 Ca</td>
<td>3.116</td>
<td>13.2</td>
<td>1 1 1 Py</td>
</tr>
<tr>
<td>2.833</td>
<td>4.8</td>
<td>0 0 6 Ca</td>
<td>2.834</td>
<td>4.2</td>
<td>0 0 6 Ca</td>
<td>2.828</td>
<td>2.4</td>
<td>0 0 6 Ca</td>
</tr>
<tr>
<td>2.482</td>
<td>11.5</td>
<td>1 1 0 Ca</td>
<td>2.485</td>
<td>9.3</td>
<td>1 1 0 Ca</td>
<td>2.480</td>
<td>8.1</td>
<td>1 1 0 Ca</td>
</tr>
<tr>
<td>2.274</td>
<td>22.5</td>
<td>1 1 3 Ca</td>
<td>2.277</td>
<td>10.9</td>
<td>1 1 3 Ca</td>
<td>2.273</td>
<td>10.5</td>
<td>1 1 3 Ca</td>
</tr>
<tr>
<td>2.087</td>
<td>15.2</td>
<td>2 0 2 Ca</td>
<td>2.086</td>
<td>8.9</td>
<td>2 0 2 Ca</td>
<td>2.083</td>
<td>10</td>
<td>2 0 2 Ca</td>
</tr>
<tr>
<td>1.910</td>
<td>11.1</td>
<td>1 0 8 Ca</td>
<td>1.906</td>
<td>12.5</td>
<td>1 0 8 Ca</td>
<td>1.906</td>
<td>10.5</td>
<td>1 0 8 Ca</td>
</tr>
<tr>
<td>1.870</td>
<td>27.7</td>
<td>1 1 6 Ca</td>
<td>1.868</td>
<td>11.7</td>
<td>1 1 6 Ca</td>
<td>1.867</td>
<td>10.5</td>
<td>1 1 6 Ca</td>
</tr>
<tr>
<td>1.621</td>
<td>4</td>
<td>2 1 1 Ca</td>
<td>1.620</td>
<td>1.8</td>
<td>2 1 1 Ca</td>
<td>1.620</td>
<td>2.6</td>
<td>2 1 1 Ca</td>
</tr>
<tr>
<td>1.599</td>
<td>5.8</td>
<td>2 1 2 Ca</td>
<td>1.600</td>
<td>4.7</td>
<td>2 1 2 Ca</td>
<td>1.598</td>
<td>3.9</td>
<td>2 1 2 Ca</td>
</tr>
<tr>
<td>1.585</td>
<td>3</td>
<td>1 0 10 Ca</td>
<td>1.582</td>
<td>1.4</td>
<td>1 0 10 Ca</td>
<td>1.584</td>
<td>1.6</td>
<td>1 0 10 Ca</td>
</tr>
<tr>
<td>1.520</td>
<td>5.1</td>
<td>2 1 4 Ca</td>
<td>1.520</td>
<td>4.5</td>
<td>2 1 4 Ca</td>
<td>1.517</td>
<td>3.1</td>
<td>2 1 4 Ca</td>
</tr>
<tr>
<td>1.507</td>
<td>4.5</td>
<td>2 0 8 Ca</td>
<td>1.506</td>
<td>2.3</td>
<td>2 0 8 Ca</td>
<td>1.467</td>
<td>1.9</td>
<td>2 1 5 Ca</td>
</tr>
<tr>
<td>1.469</td>
<td>2.4</td>
<td>2 1 5 Ca</td>
<td>1.470</td>
<td>1.5</td>
<td>2 1 5 Ca</td>
<td>1.436</td>
<td>3.3</td>
<td>3 0 0 Ca</td>
</tr>
<tr>
<td>1.436</td>
<td>5.4</td>
<td>3 0 0 Ca</td>
<td>1.437</td>
<td>3.1</td>
<td>3 0 0 Ca</td>
<td>1.417</td>
<td>2</td>
<td>0 0 12 Ca</td>
</tr>
<tr>
<td>1.421</td>
<td>2.6</td>
<td>0 0 12 Ca</td>
<td>1.420</td>
<td>6.5</td>
<td>0 0 12 Ca</td>
<td>1.521</td>
<td>10.1</td>
<td>2 1 4 Ca</td>
</tr>
</tbody>
</table>

x: calcite, Q: quartz, Py: pyrite, Gy: gypsum, Ra: rancite
mostly to be present in the meteoric-vadose zone, where the saturation index of carbonate is very high and the fluid flow is agitated (Nelson 1990). Based on XRD analysis these samples are mainly composed of calcite with a minor amount of quartz (Table 2).

2.) Second type travertine is of white to cream color and is commonly found as massive deposits in the area (Fig. 4A). Microscope observations show that they were not much affected by diagenesis, and significant amounts of mouldic, shelter and vuggy porosity have remained in rock specimens (Fig. 4B). Thin sections demonstrate that micrite, microspar and sparite are the major constituents of the rock (Fig. 4B). The microsparite and sparite calcite occurred as secondary calcite which commonly fills pores and is readily distinguishable from micrite. Since its formation, this type of travertine has been directly exposed to meteoric waters, allowing enough time for potential diagenetic alteration. However, some degree of diagenetic alteration is detectable by the presence of secondary or recrystallized calcite appearing in the vadose environment (Fig. 4B). Aggrading neomorphism of micrite into microsparite may be the result of algae and bacterial activities (Fluegel 1982). Because of aggradational neomorphism this travertine is heavier, harder, less porous and more massive than first type travertine. Recrystallization of any limestone takes place as the primary minerals equilibrate with their surroundings (Sunagawa 1990). Such changes may be driven by the polymorphic transformation of aragonite to calcite and/or the exposure of marine carbonates to meteoric water (e.g. Tucker and Wright 1990). Similar to Fall Creek Tufa (Rainey and Jones 2007) there is no indication in Ab Ask travertine that aragonite has ever been the primary deposit. Thus, the crystal size

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta^{18}O$ (VSMOW)</th>
<th>$\delta^{13}C$ (VPDB)</th>
<th>$\delta^{13}C$ (CO$_2$)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>SR T1</td>
<td>-12.58</td>
<td>6.61</td>
<td>18.92</td>
<td>-2.56</td>
</tr>
<tr>
<td>SR M 13</td>
<td>-13.02</td>
<td>6</td>
<td>17.43</td>
<td>-3.3</td>
</tr>
<tr>
<td>SR Z 14</td>
<td>-12.59</td>
<td>6.48</td>
<td>17.88</td>
<td>-2.72</td>
</tr>
<tr>
<td>SR A 22</td>
<td>-11.84</td>
<td>6.72</td>
<td>18.65</td>
<td>-2.43</td>
</tr>
<tr>
<td>SR A 12</td>
<td>-11.08</td>
<td>7.35</td>
<td>19.43</td>
<td>-1.68</td>
</tr>
<tr>
<td>SR A 15</td>
<td>-10.13</td>
<td>7.54</td>
<td>20.41</td>
<td>-1.45</td>
</tr>
<tr>
<td>SR A 60</td>
<td>-9.57</td>
<td>7.92</td>
<td>20.99</td>
<td>-0.99</td>
</tr>
<tr>
<td>SR A 9</td>
<td>-9.29</td>
<td>9.79</td>
<td>21.28</td>
<td>1.24</td>
</tr>
<tr>
<td>SR B 32</td>
<td>-6.34</td>
<td>8.14</td>
<td>24.32</td>
<td>-0.73</td>
</tr>
<tr>
<td>SR A 40</td>
<td>-11.68</td>
<td>5.8</td>
<td>18.81</td>
<td>-3.54</td>
</tr>
<tr>
<td>SR A 4</td>
<td>-12.8</td>
<td>5.16</td>
<td>17.66</td>
<td>-4.30</td>
</tr>
<tr>
<td>SR A 36</td>
<td>-14.38</td>
<td>5.95</td>
<td>16.03</td>
<td>-3.36</td>
</tr>
<tr>
<td>SR M 14</td>
<td>-12.88</td>
<td>5.97</td>
<td>17.58</td>
<td>-3.33</td>
</tr>
<tr>
<td>SR D 13</td>
<td>-12.62</td>
<td>6.06</td>
<td>17.85</td>
<td>-3.22</td>
</tr>
<tr>
<td>SR A 52</td>
<td>-7.66</td>
<td>6.4</td>
<td>22.75</td>
<td>-2.82</td>
</tr>
<tr>
<td>SR A 32</td>
<td>-6.73</td>
<td>7.96</td>
<td>23.92</td>
<td>0.94</td>
</tr>
</tbody>
</table>
and shape of calcite, porosity, and/or permeability of the Ab Ask travertine must be related to diagenesis, as described by James and Choquette (1984) for carbonates. On the basis of XRD analysis this travertine is mainly composed of calcite with a minor amount of quartz (Table 2). On the basis of its morphology and lithofacies, these travertine types are classified under the names of fissure-ridge, dam and cascade.

2-1.) Fissure-ridge travertine occurs as calcium carbonate saturation waters rise through fractures or faults, causing travertine deposition on both sides of fissures (e.g. Hancock et al. 1999). Three instances of inactive fissure-ridge travertine are exposed in the studied area of N20–30W trend (Fig. 5A). This travertine was probably formed in relation to the extensional settings similar to that of the Cambazli village area in Turkey reported by Selim and Yanik (2009). There is a fissure at the center of the travertine ridge and parallel to this fissure, laminated, hard and compact crystalline crusts are present, which can be called vertically banded travertine (Altunel 1994). The fissure-ridge travertine in the Ab Ask area is comparable with the Cukurbag fissure-ridge located close to the Pamukkale travertine deposit of western Turkey (Hancock et al. 1999).

Model studies and current observations suggest that high pressure CO₂ coming from mantle degassing and/or decarbonation of crustal carbonate rocks may accumulate in crustal traps in tectonically active regimes and induce seismicity (Chiodini et al. 2004). Faults and fractures in such an active area can provide channels for CO₂-rich hydrothermal fluids to ascend to the surface. Veins
are interpreted to be hydrothermal eruption products (Browne and Lawless 2001), which probably formed by hydraulic fracturing in response to internal overpressure of CO₂-rich fluids. The overpressure resulting from positive buoyancy of such fluids is the driving force for the propagation of hydrofractures to the surface (Uysal et al. 2009). Calcite veins occur within the pre-existing horizontally-bedded travertine and which also fills the fissures inside the ridges in the region (Fig. 5A, B). Mineralogical and textural studies show that some of these veins mainly contain calcite with an elongate blocky texture (Fig. 5C); some others are composed of calcite, pyrite, gypsum and a rather rare mineral which

Fig. 5
Pictures of veins. (A) Calcite veins filling the fissures inside the ridges in the region. (B) Veins propagating toward the surface as dyke structures within the earlier deposited bedded travertine. (C) Photomicrograph of fissure-ridge vein travertine showing elongate blocky texture of large calcite crystals, (crossed polars). (D) Photomicrograph of veins showing that they are composed of calcite, pyrite, gypsum and rancite? (crossed polars)
can be rancieite (Fig. 5D, Table 2). Similar veins to those in the Ab Ask area were reported by Uysal et al. (2009) in the fissure-ridge travertine at Pamukkale.

Microscope and SEM observations show that biological activity such as cyanobacteria (Fig. 6B) and diatoms (Fig. 6C) may have had some role in fissure-ridge travertine deposition (Fig. 6A). The small amount of silica phase, namely quartz, observed in XRD spectra, are probably the remnants of those diatom shelves which were living in such restricted hot and calcareous waters. These biological organisms could lead to carbon dioxide reduction in the environment, causing carbonate supersaturation and finally travertine sedimentation by photosynthetic activities. They have locally influenced the travertine microfabric by providing sites for the trapping and nucleation of calcite at the cell surface (Pentecost et al. 1997).

2-2.) Dam travertine is inactive and formed around the Yeyllagh Spring (Fig. 6D). This type of travertine can be distinguished from cascades by its localized vertical accretion leading to water impoundment as pools, ponds and lakes (Pentecost 2005). A large amount of plant fragments can accumulate here by water flow and later on be bound together by growing algae and coated by lime building up the dams. Well-known examples of dam travertine are the Huanglong Ravine, Sichuan, China (Pentecost 2005).

2-3.) Cascade (waterfall) travertine can form steep slopes as a result of the elevated degassing caused by the strong turbulence of water (Figs 6E, F and G). Some occurrences are active at present (Fig. 6F). They have an approximately paraboloid cross-section and are frequently accompanied by the fluted channels that have been interpreted as erosively-shaped deposits by Pentecost (2005), in which the morphology has largely been controlled by spate water trajectory. They have, however, formed as vertical falls along resistant rock layers (Dennen et al. 1990). Based on microscope studies this travertine is composed of columnar spar calcite (Fig. 6H). Columnar spars are composed of crystallites with a width of 30–50 µm and terminate in flat apices. They are also common in epigene travertine where they may be primary or the result of diagenesis (Chafetz et al. 1994). Examples include Sitting Bull Falls, New Mexico; Turners and Prices Falls, Oklahoma; the upper falls at Urach, Germany; Terni Falls, Italy, and the Huangguosho and Gaotang Falls, China (Pentecost 2005). In the UK good examples occur at Gordale and Waterfall Beck, Yorkshire (Pentecost 2005).

3.) Third type travertine (laminated travertine): This travertine type is mainly brown to yellow-brown (Fig. 7A) and is overlain by several horizons of paleosol, ash falls and quaternary alluvia (Fig. 7B) and therefore can be considered to be older than the other travertine in the area. The yellowish color of this travertine is related to its Fe₂O₃ content, which shows that it was precipitated from waters with high iron content, most probably coming directly from volcanic fumaroles and mixing with the waters, or coming from hematite-rich ash existing in the area. Laminated travertine is being exploited as ornamental stone. This lamination consists of alternating thin, dark, iron-bearing layers and thick, light,
sparitic layers, which were probably formed by interruptions in water flow (Pentecost 1999) (Fig. 7C). Lamination between iron-bearing and iron hydroxide layers of calcite could readily be explained by changes in pH within the waters from which the laminated travertine precipitated. Changes in pH at a site could be the result of: (1) changes in the composition of the waters issuing from the spring, (2) differences in the volume of water such that degassing of CO₂ (which results in pH changes) takes place closer to, or farther from, the spring, or (3) changes in the location, and thus distance, of the spring from the site of precipitation (Chafetz and Lawrence 1994). As a result, it can be concluded that, as pH increased downstream from the springs in the Ab Ask area, deposition of
Fe-oxides and carbonates must have been sequentially favored, similarly to the successive precipitation of those minerals in southern Morocco reported by Chafetz et al. (1998).

On the other hand, laminations in travertine could also form by daily or seasonal cycle in cyanobacterial metabolism (Chafetz et al. 1998). Folk et al. (1985) and Guo and Riding (1992) reported laminae from Italian travertine and attributed their origin to changes in the activity of photosynthetic bacteria due to diurnal variations in the intensity of sunlight and probably temperature. The
The mineralogical composition of yellow travertine is 95% CaCO₃ and about 5% quartz and iron oxide impurities (limonite and hematite) according to X-ray diffraction analyses (Table 2). Four major types of cement were recognized in Åb Ask laminated travertine: isopachous cement, bladed cement, drusy cement and blocky calcite cement (Fig. 8).

1.) The isopachous cement is composed of rhombohedral crystals growing perpendicular to the pore walls, and is the first cement to indicate that precipitation proceeded under phreatic conditions (Fig. 8A).

2.) The bladed spar crystal comprises weakly radiating tooth-like crystals in vertical section, and is one of the most common crystal morphologies in the laminated travertine (Fig. 8A). When these crystals are present as parallel arrays they can be described as palisades. Palisades of calcite alternating with layers of micrite are considered as clear evidence of growth interruption in laminated travertine (Fig. 8B). The presence of bladed calcite crystals in the laminated samples supports a subaqueous precipitation environment.

3.) Drusy cement is characterized by crystal size increasing from pore walls to the center of the pore spaces and could be considered as secondary cement (Fig. 8C, D). It is composed of unhedral to subhedral crystals, pore-filling but with no preferred orientation.

---

Fig. 8
Thin-section photomicrographs of laminated travertine (A) Blade calcite crystals and isopachous cement, (crossed polars), (B) Columnar-bladed calcite crystals (palisades of calcite), (crossed polars), (C, D) Drusy calcite cement (crossed polars), (E) Blocky calcite cement (crossed polars), (F) Densely clustered brown peloid aggregates (crossed polars)
4.) Blocky calcite cement is an index of phreatic burial environments (Fig. 8E). The latter cement is clearer and larger than meteoric phreatic cements.

Cement propagation is the most important diagenetic process which reduces porosity and permeability in travertine. Peloids which are observed in thin sections of laminated travertine could interpreted as a non-skeletal component of the travertine in the region. They have a spherical to ellipsoid shape, are about 300–600 µm long, with lack a of internal structure and brownish color, occurring in loosely or densely clustered aggregates (Fig. 8F). These clumps of peloids occur in a wide range of travertine and are probably microbial in origin (Pentecost 2005), or their formation might be related to algal activities (Flügel 2004).

**Stable isotope measurements**

Stable carbon and oxygen isotope compositions of travertine can provide insight into the origin (sources) of carbon and the precipitation conditions (Friedman 1970). We used the carbon isotope compositions to determine the source of the CO₂ which was dissolved in the parent waters of the travertine. Stable carbon and oxygen isotope compositions were determined for 16 samples of travertine, veins and cement. The δ¹³C and δ¹⁸O isotope values (Table 3) show broad variations. Stable isotope compositions demonstrate enrichment of the travertine in ¹³C (6 to 9.8‰ VPDB) and in ¹⁸O values (–13.0 to –6.3‰ VPDB) downstream from the hot springs, whereas δ¹³C and δ¹⁸O values of veins vary between 5.8‰ to 5.95‰ and –14.38‰ to –11.68‰, respectively.

**Discussion**

The source of CO₂ and isotopic variations in travertine and veins.

The carbon dioxide can originate from a wide range of sources, including hydrolysis and oxidation of reduced carbon, thermometamorphic decarbonation of limestone or directly from degassing of the upper mantle, mainly in areas of volcanic activity (Pentecost and Viles 1994). One frequently applied method for the determination of the origin of CO₂ is the formula:

\[ \delta^{13}C(CO_2) = 1.2 \delta^{13}C(travertine) - 10.5 \]  

This equation, which was originally proposed on the basis of a survey of Italian thermal springs and associated travertine by Panichi and Tongiorgi (1976), can be used to recalculate the original ¹³C/¹²C ratios of CO₂ from the measured δ¹³C values of fossil travertine. Using the measured δ¹³C values of travertine this formula gives the δ¹³C of the CO₂ released from the water during travertine deposition (Kele et al. 2003; Minissale 2004). As shown in Fig. 9 the carbon isotopic compositions of CO₂ and travertine at the travertine-depositing springs are expressed by this equation.

Central European Geology 55, 2012
Fig. 9
$\delta^{13}C$ of CO$_2$ vs. $\delta^{13}C$ in travertine. $\delta^{13}C$ values of CO$_2$ recalculated from $\delta^{13}C$ values of travertine according to the formula of Panichi and Tongiorgi (1976) shown at the top of the diagram.

Fig. 10
Schematic dispositional diagram of polygenic carbonates on the $\delta^{13}C$ vs. $\delta^{18}O$ (Galimov 1968; Kuleshov 1986)
Using (eq. 1) the $\delta^{13}C$ of the original CO$_2$ of the travertine and veins is about $-3.3$ to $1.25{\permil}$ and $-4.3$ to $-3.36{\permil}$, respectively (Table 3).

The $\delta^{13}C$(CO$_2$) and $\delta^{18}O$ values show that travertine and veins were probably deposited from hydrothermal metasomatic fluids (Fig. 10). Most hydrothermal karst systems owe their existence to the role of carbon dioxide, whose origin, in contrast to normal karst, is not the soil zone but deep-seated CO$_2$ sources, such as decarbonation reactions during rock metamorphism (Spötl et al. 2009).

Considering that the CO$_2$ content originating from magmatic sources generally has very low $\delta^{13}C$ values (from $-8$ to $-4$ VPDB; Craig 1963), it could be concluded that some of the veins in the area have had a magmatic source (Table 3). Applying the formula of Panichi and Tongiorgi (1976) the recalculated $\delta^{13}C$ values for travertine and some veins are more positive than the $\delta^{13}C$ value of CO$_2$ coming from a pure igneous source, obviously due to the additional heavy carbon. According to Shieh and Taylor (1969) heavy CO$_2$ can be produced through metamorphic reactions (i.e. decarbonation of carbonate rocks).

According to Fig. 11 travertine is in the range of hydrolysis of carbonate rocks, while veins are located at the boundary between the magmatic and carbonate hydrolysis domains.

The plot of $\delta^{18}O$ versus $\delta^{13}C$ shows a linear covariation trend between $\delta^{18}O$ and $\delta^{13}C$ (Fig. 12) with a high correlation coefficient ($R=0.687$). Thus, as in case of Mammoth hot spring travertine (Guidry and Chafetz 2002), the observed linear trend in Ab Ask travertine could represent:

![Graph showing the linear relationship between $\delta^{18}O$ and $\delta^{13}C$ for different types of CO$_2$.](image)

**Fig. 11**

$\delta^{18}O$ vs. calculated $\delta^{13}C$ content of primary CO$_2$ in travertine and its genesis (Milivojevic 1989) (1. Endogenic-magmatic CO$_2$ (Fournier 1981); 2. Endogenic-magmatic CO$_2$ (Blavoux et al. 1982); 3. organic and sedimentary CO$_2$; 4. CO$_2$ produced by geothermally decomposed and hydrolyzed carbonate rocks)
1.) variable mixing of waters that interacted with Paleozoic limestone aquifers, and other hydrothermal waters, as well as surface meteoric waters,
2.) long-term change in the temperature of the hot spring system, e.g. progressive heating of the system,
3.) diagenetic alteration, and
4.) a combination of all these factors.

Also, partial CO₂ and H₂O removal during progressive degassing of CO₂ and evaporation could cause a positive shift in δ¹³C and δ¹⁸O values. Low oxygen isotope values show that this travertine was deposited from high-temperature fluids. The third type travertine (laminated travertine) has enriched δ¹⁸O values (–6.34‰), which may be attributed in part to the evaporation and temperature decrease with increasing distance from the springs during precipitation.

The effect of diagenesis on the δ¹⁸O and δ¹³C values

Meteoric diagenesis mainly affects oxygen isotope values, whereas diagenesis may influence both the δ¹⁸O and δ¹³C values of travertine due to the influx of external, C-bearing fluids during recrystallization. However, the δ¹⁸O and δ¹³C values of secondary calcite in second type travertine (sample SR M14) are about –12.88‰ and 5.97‰, respectively, and in third type travertine (sample SR A32) of about –673‰ and 796‰, respectively, and thus very similar to their host travertine (Table 3). Because the carbon from travertine is transmitted to
secondary calcite with slight changes, in the case of closed systems without any additional organic carbon, the influence of diagenesis on the carbon isotope should be very low, as is observed in the present study. It could, therefore, be concluded that meteoric diagenesis, namely cementation, does not considerably affect, in such a system of pore waters of meteoric origin, the carbon isotopic composition of either the travertine or those of the cement.

Considering the observed linear trend between $\delta^{13}$C and $\delta^{18}$O values in the Ab Ask travertine (Fig. 12), it is likely that the fluids responsible for the formation of this travertine and these veins are mixtures of fluids (for example meteoric and hydrothermal waters) of different origins. Carbonate formations have undergone a continuous decarbonation process as a result of the reaction of CO$_2$-rich hydrothermal fluids with these rocks. These fluids contained CO$_2$ gas released through hydrolysis of the carbonate rocks and carried to the surface with the emerging thermal springs, precipitating travertine due to rapid degassing of CO$_2$, partly due to biological activities. The drop in the partial pressure, while raising the fluids to the surface, leads to a decrease in the solubility of CO$_2$ in water and, ultimately, veins are precipitated in the fracture zones due to rapid CO$_2$ degassing.

Effective factors controlling the $\delta^{13}$C values

As was observed, all types of travertine and veins have relatively high $\delta^{13}$C values. According to Kele et al. (2011) high $\delta^{13}$C values of Pamukkale travertine has been attributed to two different sources: 1) contribution of CO$_2$ liberated by thermometamorphic decarbonation of carbonate rocks and 2) magmatic CO$_2$ which was revealed through He isotopic studies of Gülec et al. (2002).

High $\delta^{13}$C values (between 6 and 9.79‰) of Ab Ask travertine could also be attributed to the contribution of heavy CO$_2$ (rich in $^{13}$C) liberated during thermometamorphic decarbonation of carbonate basement rocks (most probably Mesozoic limestone). High-temperature thermometamorphic processes are usually related to the areas of elevated geothermal activity, such as travertine in Fiano Romano with $\delta^{13}$C values between 6 and 9‰ VPDB, and Yellowstone thermal springs with $\delta^{13}$C values between 3 and 8‰ VPDB (Craig 1963) which are related to the carbonate rocks existing in the substrate. During rapid degassing of CO$_2$ from thermal waters, non-equilibrium isotope fractionation can occur and as a result, heavy carbon isotope becomes concentrated in the precipitated travertine (Pentecost 2005). The isotopic composition of carbonates precipitating from water is also affected by the activity of blue-green algae, which are widespread on the surface of travertine. The photosynthesis process results in the
preferable consumption of CO$_2$ with the light carbon isotope by plants (Guo et al. 1996).

Based on the origin of the CO$_2$ interacting with the groundwater, Pentecost (2005) subdivided travertine into meteogene and thermogene or thermal deposits. Meteogene travertine (i.e. calcareous tufa) generally shows a negative carbon isotopic composition ($\delta^{13}C$ vs. VPDB between –11 to 0‰) reflecting the depleted $\delta^{13}C$ of soil CO$_2$ (Deines 1980). Thermogene travertine, on the other hand, values of $\delta^{13}C$ vs. VPDB in the range –1 to 10‰ (D’Alessandro et al. 2007). According to geologic observations and isotopic analysis obtained for the present study, the Ab Ask travertine can be regarded as thermogene travertine and is comparable with the Viterbo and Rapolano Terme travertine in Italy (Fig. 13). Waters responsible for these deposits are normally hot and carry CO$_2$ coming from the interaction between hot rock and CO$_2$-rich fluids (Ohmoto and Rye 1979).

**Conclusions**

Travertine deposits in the Ab Ask area were studied using combined petrographic, mineralogical and stable isotope analysis. Based on their sedimentation sequence and lithofacies, travertine is categorized into three main types of first (stream channel deposits), second and third type (laminated) travertine. First type travertine consists of fresh and recent carbonate sediments in the streams and channels from hot water. Second type travertine consists of white to cream-colored, massive deposits which, based on their morphology and lithofacies, are classified into four kinds as fissure-ridge, dam, cascade, and blocky types. Third type travertine consists of laminated travertine, having undergone high to moderate diagenesis, of yellow to brown color. XRD analysis showed that the travertine is composed of almost pure calcite with minor amounts of quartz, whereas veins contain some amounts of pyrite, gypsum and rancite in addition to calcite. Diagenetic features in second and third types of travertine (laminated travertine) led to distinguishing two burial and meteoric diagenesis environments. Based on carbon and oxygen isotopic analysis of travertine a linear trend was observed between $\delta^{13}C$ and $\delta^{18}O$ values with increasing distance from hot springs, which is attributed to the mixing of two or more different fluids.
There is a significant enrichment in δ¹³C values of all travertine types due to decarbonation of limestone, algae activity and rapid degassing. Isotopic studies reveal that the travertine of the Ab Ask area may be of thermal water origin and therefore belong to the thermogene travertine category.

Acknowledgements

The authors thank the Research Council at the University of Tehran for supporting the present study. We are grateful to Dr Sándor Kele and Dr Enrico Capezzuoli for their constructive and fruitful comments to improve the paper.

References

Alavi, M. 1996: Tectonostratigraphic synthesis and structural style of the Alborz Mountain system in Northern Iran. – Geodynamics, 21, pp. 1–33.


Allenbach, P. 1966: Geologie un Petrographe des Damavand und seiner Umgebung (Zentral Elburz), Iran. – Mitteilungen, Geologisches Institut, ETH und Universität Zürich, Neue Folge 63, pp. 1–144.


Mineralogy and geochemistry of the Ab Ask travertines in Damavand geothermal field, Iran


Galimov, E.M. 1968: Geokhimiya stabil'nykh izotopov ugleroda (Geochemistry of Carbon Stable Isotopes), Moscow: Nedra.


Kuleshov, V.N. 1986: Izotopnyi sostav i proiskhozhdenie glubinnykh carbonatov (Isotopic Composition and Origin of Deep-Seated Carbonates), Moscow – Nauka.


Minissale, A. 2004: Origin, transport and discharge of CO₂ in central Italy. – Earth-Science Reviews, 66/1–2, pp. 89–141.


Rainey, D.K., B. Jones 2007: Rapid cold water formation and recrystallization of relict bryophyte tufa at the Fall Creek cold springs, Alberta, Canada. – Canadian Journal of Earth Sciences, 44, pp. 899–908


Central European Geology 55, 2012
Uysal, T., Y. Feng, J. Zhao, V. Isik, P. Nuriel, S.D. Golding 2009: Hydrothermal CO2 degassing in seismically active zones during the late Quaternary. – Chemical Geology, 265, pp. 442–454.