

Petrography and geochemistry of Quaternary travertines in the Ab-e Ask region, Mazandaran Province- Iran

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Abstract

The travertine deposit springs are located on the southeast of the Damavand Volcano, 85 km northeast of Tehran Province. The deposits of these springs mainly outcropped with cascade, hill, conical, layered, calcareous Tufa and Fissure-Ridges morphologies. Travertine studies have usually been conducted based on field observations, geochemistry and hydrology. The tectonic activity of the region, faults and fractures have provided some channels for the rise of CO₂-rich hydrothermal fluids. The present study was carried out based on field, geochemical and hydrological surveys. The results of thin section and SEM analyses show that photosynthetic microorganisms such as blue-green algae and diatoms play a key role in the formation of these travertines. Field studies alongside with petrographic characteristics revealed presence of crystalline crust, rafts, foam, laminated and tufa lithofacies. The mineralogy of these lithofacies is calcite. There is a significant enrichment in $\delta^{13}\text{C}$ values of all travertine types due to decarbonation of limestone. Based on the isotope, performed on travertines of the region, the linear trend observed between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values is attributed to the mixture of two or more different fluids. This enrichment is attributed to the de-carbonation of limestone, algae activities and rapid de-saturation of hot springs.

Keywords: Ab-e Ask, Travertine, Lithofacies, Geochemistry, Tufa.

Introduction

Travertines are of a large group of non-marine carbonate deposits associated with freshwater springs, lakes, caves and karst systems, which extend in most parts of the world (Fig. 1). Hot and mineral springs are usually formed in places where the morphologic, tectonic, magmatic and atmospheric conditions are provided. In fact, these rocks are formed by the deposits from freshwater springs due to organic and inorganic activities (Chafetz & Folk, 1984).

In general, during the formation process of travertine deposits, hot water passes through the levels of carbonate rocks, especially limestone, and because of its acidity, dissolves calcium carbonate in these rocks and transmits it as carbonate and bicarbonate solutions to the ground. Changing the conditions of deposition in the springs can interrupt the formation of these travertine layers, resulting in the formation of a separation layer between the travertine layers (Chafetz & Folk, 1984; Ford & Pedley, 1996; Brogi & Capezzuoli, 2009). Travertines generally have different hydrological systems at the global level, but the origin of these deposits is generally related to tectonics and tensile fault systems (Hancock *et al.*, 1999).

The present study aimed to investigate the

morphology, texture changes and mineralogy of Ab-e Ask travertine deposits based on geochemical, hydrochemical and isotope data. The data of present study were collected using field survey, petrographic study and the results of geochemical analyses.

Geological setting

This area is located in the 1: 100,000 geological map of Damavand (Fig. 2). The Alborz Mountain chain, in the southern part of the Caspian Sea, has about 600 kilometers length with an east-west trend and more than 100 kilometers width. In this area, there are several peaks with the height of more than 4000 m (Ehteshami-Moinabadi & Nasiri, 2017). The Ab-e Ask region is located in the southeast of Damavand volcano. Travertine deposits from the currently active and quaternary springs in Ab Ask region are mainly located on the Paleozoic, Mesozoic formation to volcano- clastic quaternary deposits (Fig. 2, 3A and 3B).

The lithological composition of the Paleozoic formations in the region consists of dolomite, limestone, sandstone related to the Mila (Upper Carboniferous) and Doroud Formation (Permian), carbonate rocks related to the Elika (Triassic) and Lar Formation (upper Jurassic) as well as

sandstones and shales containing vegetable fragments of the Shemshak Formation (middle Jurassic). The volcano-clastic sequences of Damavand volcano, in the form of lava and ashes during its activities in the quaternary period, were suitable beds for the formation of travertine deposits.

Based on numerous geological evidences, this area is tectonically active and due to the activity of existing faults, the rock units from the former eras are placed against the shales and sandstones of the Shemshak Formation and have provided a suitable structure for the appearance of travertine deposit spring in this area.

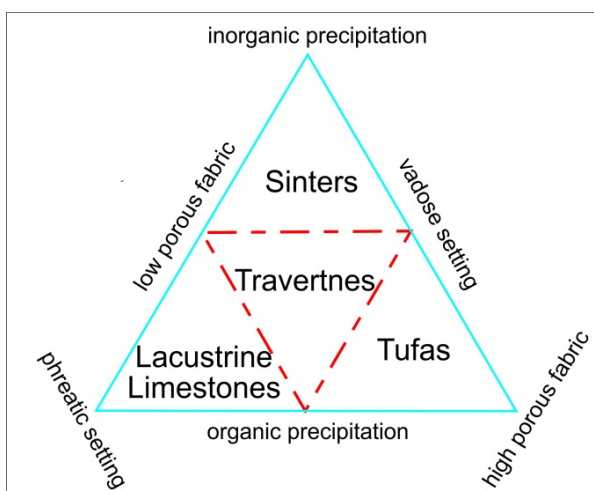


Figure 1. Genetic relationship between different categories of non-marine carbonates (Kobana & Schweigert, 1993).

There is a close relationship between the formation of travertine and faulting, which is a main mechanism for the transfer of hot springs from the depths to the surface. Travertines is a term used to emphasize the relationship between the travertine sedimentation and the faulting. It suggests that travertine age can be greatly considered as an index for the fault age (Hancock *et al.*, 1999; Rahmani *et al.*, 2011).

Factors such as increased temperature, reduced pressure, physical disturbances such as water turbulence, photosynthesis by aquatic plants, fractures, and faults with microbial activities cause deposition of travertine by removing CO₂ from water. Travertine can be divided into two Meteogene and Thermogene groups based on the source of CO₂ reacting with groundwater (Pentecost, 2005). In meteogene travertines, the source of CO₂ is superficial and formed by organic

activities in the soil. In thermogene travertines, the source of CO₂ is deep and results from hydrolysis, oxidation, carbon reduction, de-carbonization of limestone or directly from the upper mantle (carbonatites).

Thermogene travertines are found mainly in volcanic and fault areas along with hydrothermal minerals. Existing layers are the results of gradual or immediate changes in the color and composition of travertines due to changes in recent control factors (Fig. 4) (Burnside, 2010; Kele *et al.*, 2008).

Material and methods

In present study, the role of various factors in the formation of travertine in the Ab-e Ask region was investigated. To do this, the morphology of travertines was studied through field survey, and the travertines along the path of hot springs and the older ones were sampled. During the preparation steps, samples were washed with distilled water to remove contaminants. After drying the samples, thin sections were prepared and petrographic study was performed on them. To detect photosynthetic microorganisms, samples were studied using scanning electron microscopy (SEM). X-ray diffraction analysis was performed on powdered rock reference samples to determine the mineralogical composition of fissure-Ridges travertine and travertine veins. 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) and with a precision of 0.2% and according to PDB standard. Moreover, XRD analyses were performed on samples at the Institute for Studies in Theoretical Physics and Mathematics (IPM) of Damghan University and SEM analysis the University of Tehran.

Types of travertines based on morphology and formation environment

To name travertines, various classifications have been proposed based on the origin, morphology and travertine texture. According to Pentecost (1995a), travertines are divided into eight groups in terms of morphology and formation environment:

1. Mounds, 2. Fissure-Ridges, 3. Fall, 4. Dam, 5. flow layers with oncoids, 6. Lake, 7. Marsh and 8. Cemented rudite travertines.

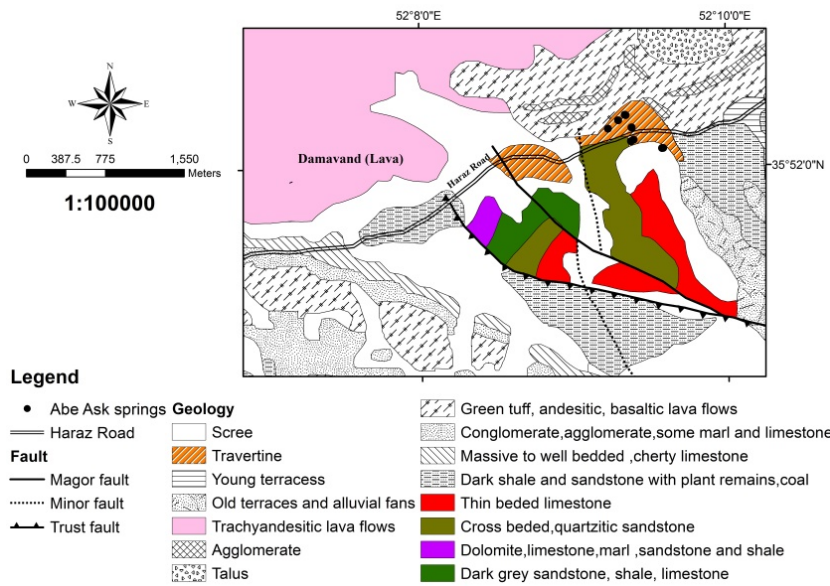


Figure 2. Simplified geological map of the Haraz Valley at north of Tehran (Allenbach & Shteiiger 1966).

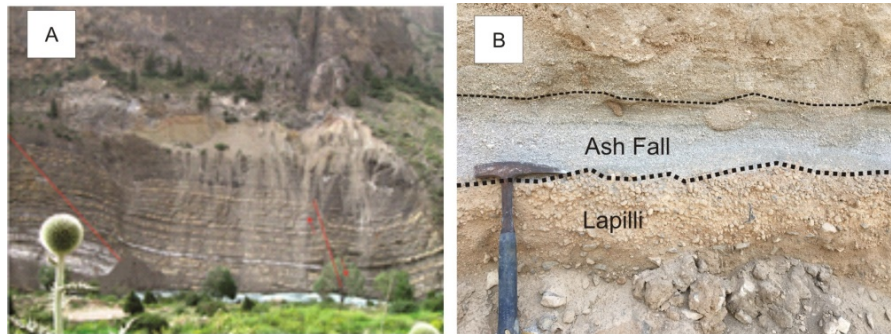


Figure 3. (A) Alteration of collapse deposits, including ash and lapilli on laminated travertine in the eastern part of Ab-e Ask travertine mine. (B) The alternative Shemshak Formation is composed of layers of shale and sandstone, which are located beneath the ashes and lavas.



Figure 4. Panoramic photo of an active the Ab-e Ask travertine mine in the southeast of Damavand Peak.

The exodus of calcareous springs along faults and fractures leads to deposition of calcareous sediments on the earth's surface. These sediments have different geomorphological forms. Regarding field observations, morphology of the deposits of the Ab Ask calcareous springs includes: 1- Cascades, 2- Hill and conical, 3-Layered, 4- Calcareous Tufa and 5 - Fissure-Ridges travertines.

1. *Cascade travertines*: A part of the deposition of travertines is seen as successive beautiful cascades. This type of travertine has been formed on surfaces with steep slopes due to the drop in flow rate and water pressure and has been developed at variable intervals from the span of the spring and is massive. Due to the presence of iron oxides and also the coverage of mosses and algae, these travertines are of an interesting color variation (Fig. 5A).

2. *Hill-conical travertines*: This type of travertine is formed by the flow of spring on sloping surfaces lacking a barrier on the surface (Fig. 5B).

3. *Layered travertine*: Existing structures in the travertine morphology of the area include a simple strip structure, a wave strip that is usually formed simultaneously with the formation of deposits (Fig. 5C). Usually deposition of iron compounds begins

sooner than carbonates, so the iron concentration in travertine decreases, which is concurrent with the reduction in the concentration of other elements. Laminations indicate a lag or loss of fluid flow that is considered as the evidence of periodic variations in deposition rates. In these deposits physicochemical phenomena are superior to biochemical ones and includes] evaporation, turbulence and temperature parameters. In laminated travertine samples, sparry calcite crystals usually have a subtle zoning, which is a result of a small change in the amounts of iron and manganese. This zonation is formed due to the fact that carbonates and iron hydroxide are not deposited simultaneously from the mineral springs, so a certain mineralogical zonation is formed in travertine deposit spring. Due to existing layers of volcanic ashes above travertine, it is likely that the iron oxide resulting in different colors of travertines has the exterior origin and this may be associated to the alteration of iron and magnesium minerals of the ashes. The concurrence of final activities of Damavand volcano with the formation of travertines can be considered as the main cause of these volcanic ashes.

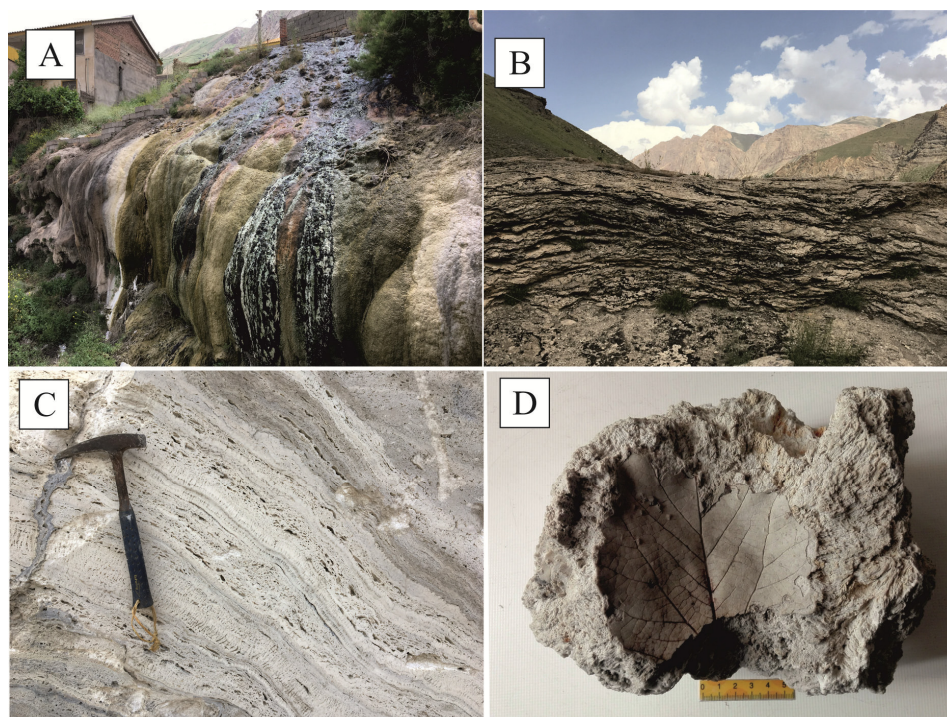


Figure 5. (A) Active cascade travertine with coverage of mosses and algae. (B) Hill-conical travertine, fissure - ridge travertine-stack (C) close-up of cut surface of laminated travertines and (D) calcareous tufa with plant remains in tufa deposits with high porosity in the course of spring.

4. *Calcareous Tufa*: These deposits refer to highly porous sponge deposits deposited around the springs in the region and the Haraz River. Pedley (1990) also defines tufa as sponge or porous carbonates. In fact, tufa is a highly porous, calcareous rock formed by the deposits from water at ambient temperature. Tufa develops on a variety of underlying layers. These deposits have less porosity than travertines, and the plant remains such as the leaves of plants adjacent to the spring or the bushes in the course are usually seen with these deposits. Tufa is sometimes known as meteogene travertine (Fig. 5D).

5. *Fissure-ridge travertines*: There is a close relationship between the formation of travertines, tectonic activity as well as faulting, which is the main mechanism for the transfer of hot springs to the earth's surface. Typically, this type of travertines is primarily formed on hanging wall segments of normal fault or in shear zones in relation to strike slip to oblique slip movement (Altunel & Hancock, 1993a; Hancock *et al.*, 1999; Atabey, 2002). The formation of these travertines is that the calcium carbonate-saturated water rises up from the central ridge and causes the travertine to be deposited on the wall of the ridge and also on its sides, resulting in a linear fissure. This morphology is more likely to be observed in older deposits (Fig. 6A). If the flow rate from the central ridge is high, the fissure would have low height and wide width, but if the flow rate is low, the travertine deposits further around the central ridge, resulting in a fissure with high height and low width (Fig. 6A) (Bargar, 1978; Chafetz & Folk, 1984; Pedley, 2009). Given the fact that Ab Ask region is an active tectonic and seismic zone, due to fractures and faulting resulting from it, CO₂-rich

hydrothermal fluids have outcropped as veins into fissure-ridge travertine. During the spring of 1998, a huge landslide took place in the Haraz valley, near Ab-e Ask village, causing the road to be closed and destroying 600 meters of the road. This landslide was accompanied by falling and slipping of the rocks (Ehteshami-Moinabadi & Nasiri, 2017) (Fig. 6B).

The results of SEM analysis also show that biological activities such as photosynthetic bacteria and diatoms have a direct relationship with the deposits of fissure-ridge travertine in the case study. Only heterotrophic bacteria and archaea microorganisms can live in hypothermal hot springs at temperatures above 75°C, while all herbal groups, bacteria and fungi can live in areas where the water temperature is below 40 °C (Jones and Renaut, 2010) (Fig. 7A, B).

Petrography and diagenesis of travertine

The petrography of the studied travertines shows various fabrication and textures. Porosity and lamination in microscopic and macroscopic samples are of the most important appearance features of the travertine in the region. The context or matrix of most travertines are mostly fine-grained and dark-colored and is known as micrite matrix. The results of travertine pyrography showed the dark micrite lamination and sparry calcite laminates that were formed alternately. The changes observed in these layers are often attributed to seasonal variations, and calcite deposition is related to the concentrations of dissolved calcium carbonate during the warm months. The sparite cement observed in the cavities is the result of dissolution and re-deposition (Atabey, 2002).

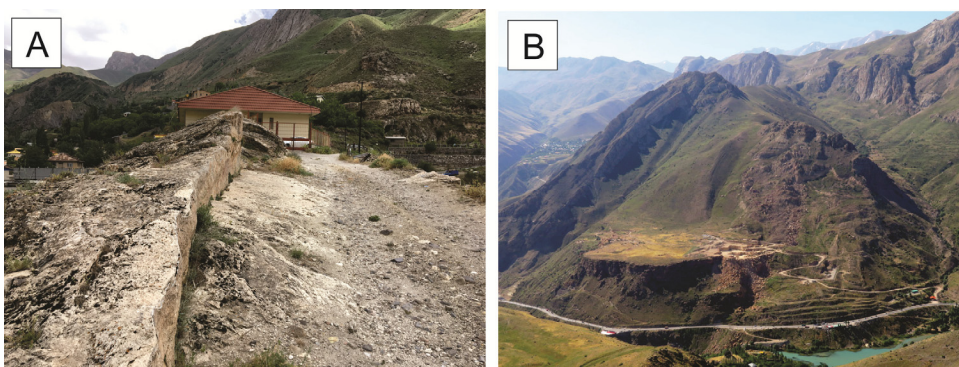


Figure 6. (A) Deposits of fissure-ridge travertines in the Ab-e Ask region. (B) Panoramic photo of landslide location in the area of the Ab-e Ask travertine mine (Ehteshami-Moinabadi & Nasiri, 2017). The travertine mine is located near the landslide, adjacent to the Ab-e Ask village.

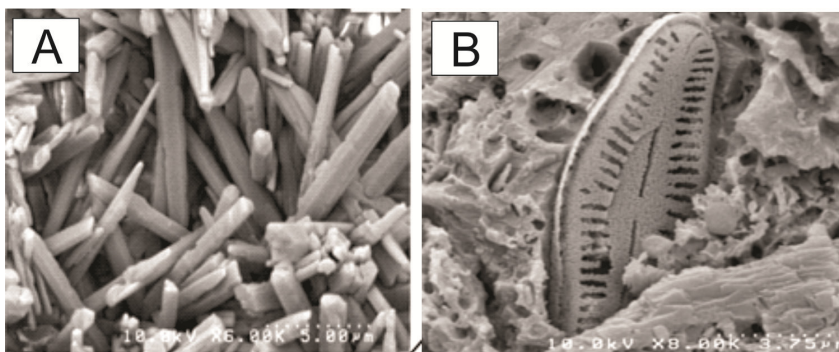


Figure 7. (A) SEM images of needle-like calcite crystals (B) fossil of diatom in fissure-ridge travertines.

The most common diagenetic phenomena in travertines of the case study are the dissolution and cementation. Porosities are formed as primary porosity, which is concurrent with deposition and secondary porosity after diagenesis. These porosities are more common as cavities. Available cements are in block and form of sparry calcite cement. Five types of lithofacies were identified in travertine deposits in the Ab-e Ask Region based on common ground-scale morphologies region and hand specimens:

1- Coated bubble gas boundstone lithofacies, 2- Raft boundstone lithofacies, 3- Crystalline crust lithofacies, 4- Mudstone-boundstone microsparite lithofacies and colloidal-peloidal texture, 5- Laminated-dendrites boundstone lithofacies.

Coated bubble gas boundstone lithofacies

This type of boundstone is seen in cream to brown. It is surrounded by hollow spheres with carbonate coating. The coating is of micrite to microsparite families, and the space between the bubbles is filled with sparry calcite cement. These travertines are mainly in brown or brownish yellow due to impurities of iron oxide. At the surface of this travertine, there is a coating of fine gas bubbles, possibly due to gas escape and photosynthesis, which is called the Foam Rock (Fig. 8A and 8B).

Raft rudstone lithofacies

This kind of lithofacies is macroscopically in white to cream and has a high primary porosity. The raft deposits are microscopically micrite/ sparry micrite laminates. Under the microscope, the contexts of most samples are from micrite to microsparite, and in some cases, it shows only a micrite context. Micrite is seen as dark areas with vague bands and in microbial or cement-like shape. Microbial micrite are mainly the result of microbial activity (Fig. 9A and 9B).

Crystalline crust lithofacies

This type of lithofacies is mainly formed around the span of spring, and is mainly an alternation of light layers of sparry calcite crystals and dark micrite layers (Atabey, 2002). Sometimes calcite and aragonite have grown in a string or chip forms, perpendicular to the layers of micrite layers (Fig. 10A). This lithofacies is in fan form, and in the polarization light, the crystals exhibit undulatory extinction. The observed micrites observed in this facies is the same microbial deposits caused by the activity of algae and bacteria. The micrites are deposited around bacterial colonies and around algae, especially cyanobacteria (Janssen *et al.*, 1999). The formation of this lithofacies is mainly due to rapid deposition of high velocity flows on smooth slopes, margins and vertical walls of the terraces and walls of the ponds. The thickness of this lithofacies ranged from several centimeters to greater than tens of centimeters (Fig. 10 A and B).

Mudstone-boundstone microsparite lithofacies and clotted-peloidal texture

In this lithofacies, the micrites are observed as clotted micrites, which are called clotted texture. In most thin sections, the micrites are dark, and form opaque areas with uncertain to certain boundaries. The clots are in the form of micrites in light sparite crystals (Fig. 11).

Laminated-dendrites boundstone lithofacies

The term bush was first used by Kitano (1963) to describe the structures of Japanese travertines, and then by Chafetz & Guidry (1984) to study on travertine deposits in Italy. They also recognized three types of bushes (bacterial, crystalline, and radial crystals). Complex structures are created by joining or bounding bushes upward and eventually bush branches are created. Naturally, the branches have radial or tree-like structures, each of which has

a height ranged from less than 1 mm to several centimeters. The kind of these branches includes micrite or sparite or both. Algae branches are more associated with cold meteogene travertine (Pentecost, 2005). The in-place travertine facies

(including plant and bacterial) are of the boundstone group (Ferreri, 1985). Dendritic forms of calcium carbonate are more commonly found in thermogene travertine. These lithofacies are formed during the deposition on small slopes (Fig. 12).

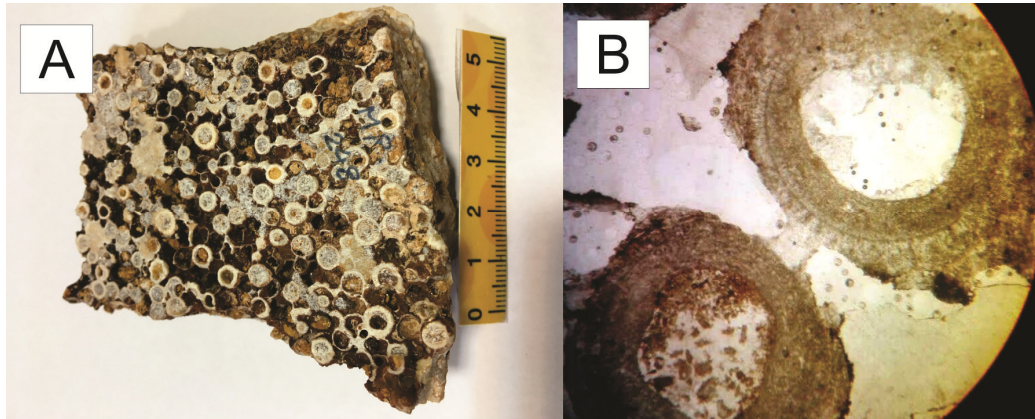


Figure 8. (A) A coating of gas bubbles in a hand specimen of the laminated travertine surface, produced by the gas escape (B) Bubbles with micrite laminated coating that the space between them is replaced by sparry cement (plane-polarized light).

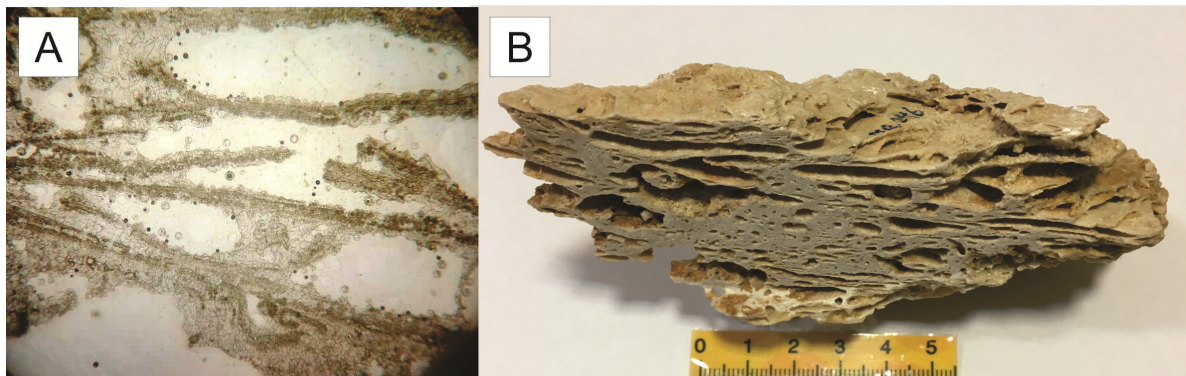


Figure 9. (A) The microscopic section of the passages with cavity porosity (plane-polarized light). (B) Welding of the rafts, and the formation of germination in the manual sample.

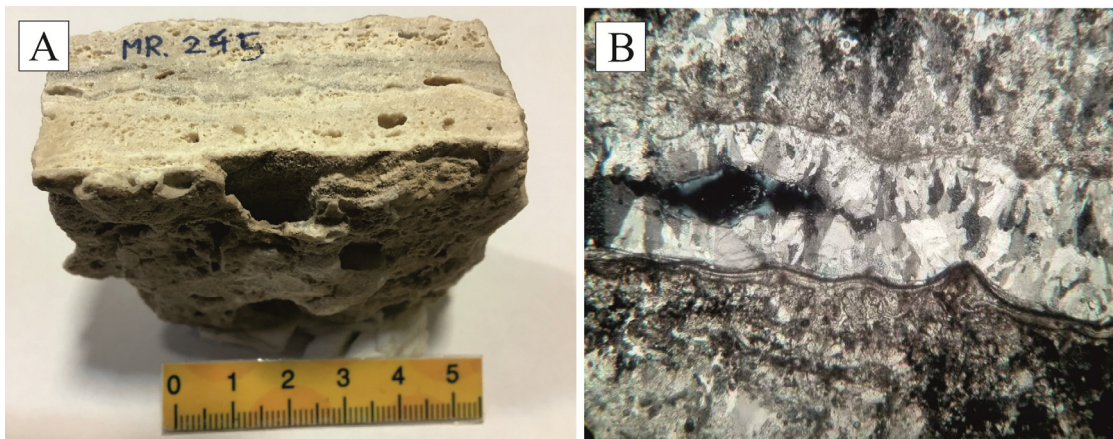


Figure 10. (A) Crystalline crust lithofacies in a hand sample. (B) Calcite crystalline in radial- string form with undulatory extinction (crossed-polarized light).



Figure 11. Clotted texture with the distribution of clotted micrites grains (crossed-polarized light).

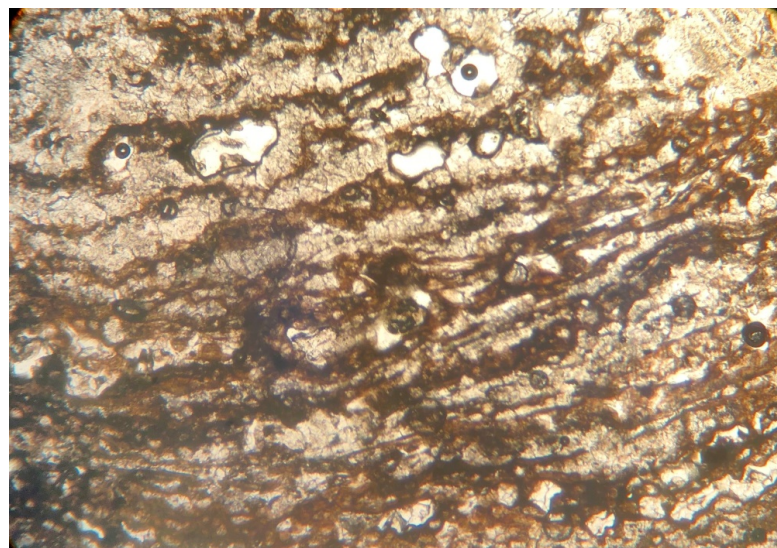


Figure 12. Alteration of algae laminates with calcite crystals in radial-branch form with undulatory extinction (crossed-polarized light).

Mineralogy of travertine deposits based on microscopic studies and XRD analysis

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. The Ab-e Ask travertine's are composed of 95% calcite and less than 5% of quartz and iron oxide, pyrite, gypsum and ranciete impurities (Fig. 13A and B).

Physico-chemical properties of Ab-e Ask springs

There are 9 springs on *both sides of the* Haraz River. These springs come from Jurassic limestone rocks, leading to the deposition of travertines in some of them. Their water contains calcium

bicarbonate with acidic pH and sulfur. Figure 14 is a view of one of the springs in Ab-e Ask village.

The chemical and physical composition data of the travertine deposit spring in Ab-e Ask region are listed in Table 1. The Ab-e Ask hot springs all have an almost identical temperature (23 to 32 °C), and their pH is nearly neutral and more or less acidic and between 6 and 6.6. The EC of water is between 1.39 to 3.64 ($\mu\text{mho} / \text{cm}$).

One of the common methods used for determining the type (hydrophilic facies) of water is to use Piper's chart (Piper, 1944), which is based on the determination of main anions and cations of the water. Piper's chart of the Ab-e Ask hot springs is plotted and presented by Ansari (2013) (Fig. 15).

Table 1. Physicochemical parameters of Ab-e Ask hot springs (Ansari, 2013).

Spring name	PH	Chemical and physical composition data of Thermal springs from Damavand area.										
		EC μs/cm	HCO ₃ mg/l	Cl mg/l	SO ₄ mg/l	K mg/l	Na mg/l	Mg mg/l	Ca mg/l	Fe mg/l	SiO ₂ mg/l	Temp. (°C)
Larijan	6.5	1100	167.77	10.64	330.45	3.13	18.85	24.05	129.26	0.9	42	60
Strabaku 1	6.1	2700	671.11	166.6	902	13.69	110.58	77.82	444.8	1.5	24	33
Strabaku 2	6	4000	915.15	283.68	1404.8	21.51	165.53	83.9	691.38	1	32.5	32
Strabaku 3	5.5	4000	658.91	383.6	1395.7	21.51	165.53	94.85	637.27	0.65	33	31
Strabaku 4	6.2	4000	686.36	383.68	1406.8	21.51	165.53	84.51	654.3	1.75	33	32
Ask e Nadaali	6.6	3160	1256.8	426.5	101.8	27.3	229.9	3655	376.6	1.2	17.5	28
Ask e Zagh	6.7	3002	1134.7	437.9	98.9	27.3	229.9	67.4	322.6	0.91	15	25
Ask e Sare Pol	6	3111	1238.5	400.7	95.5	29.3	211.5	51.6	370	1.04	16.5	32
Ask e Pashank	6.8	2600	793	117	106	28	215	731	680	0.5	26.7	31
Polor	7											
* : not measured		78	13	0.75	10	5	32	*	*	*	*	5

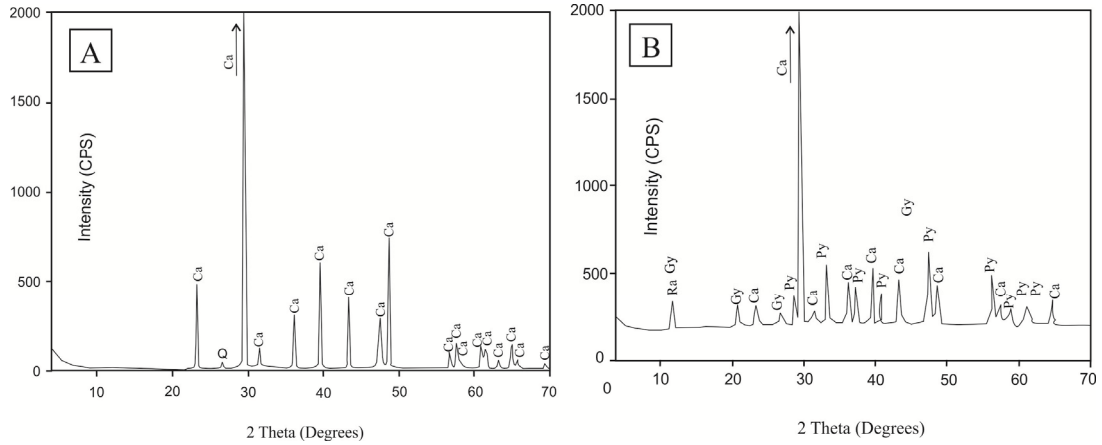


Figure 13. (A and B) X-ray diffraction of laminate travertine with compounds of calcite (Ca) and quartz (Q) pyrite (Py), gypsum (Gy) and ranciete (Ra) are shown in the chart.



Figure 14. A view of one of the springs in the Ab-e Ask village.

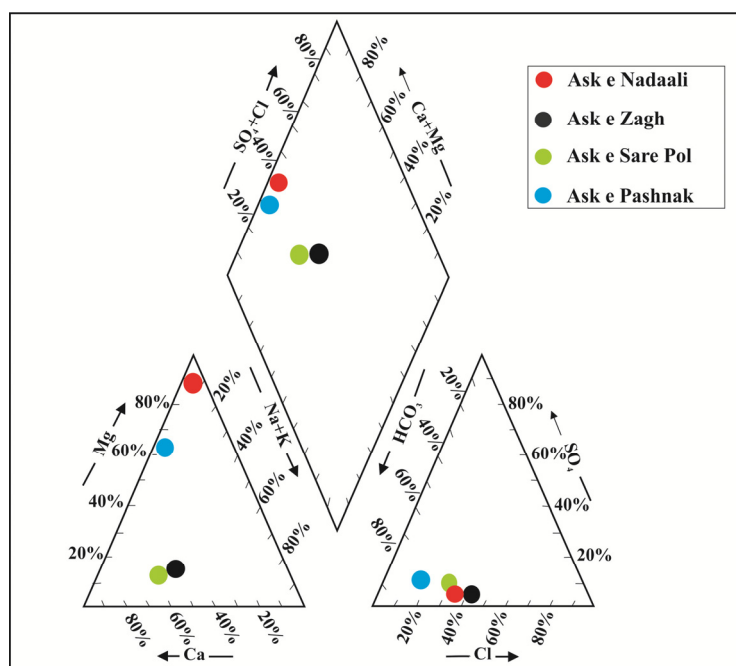


Figure 15. Piper's triangular diagram related to the water quality of some the Ab-e Ask springs (derived from Ansari (2013) after applying the changes).

This chart shows that calcium is the dominant cation in Ab-e Ask hot springs (except for Ask-e Nadali and Ask-e Pashnak springs, which are rich in Mg). The relative concentration of anions indicates that the Ab-e Ask springs are divided into two groups based on anionic changes and water chemistry such as HCO₃ and SO₄. The Piper's chart plotted using cations and anions of the samples from hot springs show that the water chemical composition of each spring is influenced by the kind and type of rock units where springs come from. Ask-e Zagh and Ask-e Sarpol hot springs emerged in the Jurassic carbonate rocks of the area and Ask-e Nadali and Ask-e Pashnak in the Basaltic prisms and lava in the area (induced by Damavand andesitic trachyte and basalt trachyte eruptions).

Giggenbach (1991) used the relative participation of Cl, HCO₃ and SO₄ as a primary indicator to investigate the mixture of geothermal fluid with cold groundwater (Fig. 16). The samples studied in present research are located on the HCO₃ side and within the range of peripheral and shallow waters, indicating the absorption of scattered CO₂ from lower levels into underground waters or from magmatic activities (Al-Kohlani, 2008). Ansari (2013) believes that the placement of samples in the range of ground and peripheral water is related to the rotation of surface water in sedimentary and volcanic rocks. In all Ab-e Ask springs, HCO₃

(117-426 mg / l) is a dominant anion. The increase in HCO₃ is due to the reaction between dissolved carbon dioxide and the host rock forming HCO₃. In Ab-e Ask hot springs, except for Ask-e Nadali and Ask-e Pashnak springs, Ca > (Na+Mg+K) and HCO₃ > (SO₄ + Cl) while in Ask-e Nadali and Ask-e Pashnak springs, Mg > (Na+Mg+K) and HCO₃ > (SO₄ + Cl), which can be justified by the emergence of them in basaltic rocks in the region. Displaying water chemistry data on the Giggenbach's (1991) chart and their placement in the range of ground and peripheral water, on the one hand, reflects the absorption of carbon dioxide by intrusive surface water that intrudes into the springs through the fractures and faults or the channels and also related to magmatic activities in the region. Another theory referring to the rotation of surface waters in sedimentary and volcanic rocks confirms the results from the Piper's chart.

Isotope Characteristics of Carbonate Deposits

One of the most common methods used for determining the primary origin of CO₂ released from water during deposition of travertine is the use of (equation 1). This equation, for the first time, was used by Panichi and Tongiorgi (1976), in their study on the hot springs of Italy and its associated sediments (Table 2).

$$\delta^{13}C_{(CO_2)} = 1.2 \delta^{13}C_{(travertine)} - 10.5 \quad (1)$$

In order to determine the origin of CO₂ of the Ab-e Ask springs, the δ¹³C and δ¹⁸O analyses were performed on travertine samples (Table 2). For these samples, the δ¹³C values ranged about from +6.8 to +9.8 per mils and δ¹⁸O values from -0.13 to -9.9 per mils, according to the VPDB standard; therefore, these travertines indicate enrichment in δ¹³C value and depletion in δ¹⁸O value. According to Rollinson's chart (1993) on which the δ¹³C isotope composition of the primary CO₂ of the fluids causing travertine decomposition is plotted against δ¹⁸O, the samples are located within the hydrothermal fluid range (Fig. 17). The hydrothermal calcite resulting from the interactions between water and rock in the mid-oceanic ridges

indicates the mixture of mantle carbon (M) and sea water carbon (S) (Stack and ONeil, 1982); therefore, according to this chart, the CO₂ in the Ab-e Ask travertine deposit spring has two marine and mantle sources. The Relatively high δ¹³C values can be due to an unbalanced fractionation during a rapid degasification of dissolved CO₂ (rich in ¹²C) (Uysal *et al.*, 2009); but it should be noted that this process cannot be solely responsible for very high values of δ¹³C in the studied travertines. Due to the photosynthetic activity of microorganisms such as algae around these springs, these microorganism seems to be one of the reasons for increasing the value of carbon isotope up to ‰9 (Rahmani Javanmard *et al.*, 2012).

Table 2. Stable oxygen and carbon isotope data and recalculated δ¹³C (CO₂) values of travertine and veins from the Ab-e Ask geothermal field.

Sample	δ ¹⁸ O (VPDB)	δ ¹³ C (VPDB)	δ ¹⁸ O (VSMOW)	δ ¹³ C (CO ₂)	Description
SR T1	-12.58	6.61	18.92	-2.56	First type travertines
SR M 13	-13.02	6	17.43	-3.3	Second type travertines
SR Z 14	-12.59	6.48	17.88	-2.72	Second type travertines
SR A 22	-11.84	6.72	18.65	-2.43	Second type travertines
SR A 12	-11.08	7.35	19.43	-1.68	Second type travertines
SR A 15	-10.13	7.54	20.41	-1.45	Second type travertines
SR A 60	-9.57	7.92	20.99	-0.99	Second type travertines
SR A 9	-9.29	9.79	21.28	1.24	Second type travertines
SR B 32	-6.34	8.14	24.32	-0.73	Third type travertines
SR A 40	-11.68	5.8	18.81	-3.54	Veins
SR A 4	-12.8	5.16	17.66	-4.30	Veins
SR A 36	-14.38	5.95	16.03	-3.36	Veins
SR M 14	-12.88	5.97	17.58	-3.33	Cement (Secondary calcite)
SR D 13	-12.62	6.06	17.85	-3.22	Cement (Secondary calcite)
SR A 52	-7.86	6.4	22.75	-2.82	Cement (Secondary calcite)
SR A 32	-6.73	7.96	23.92	0.94	Cement (Secondary calcite)

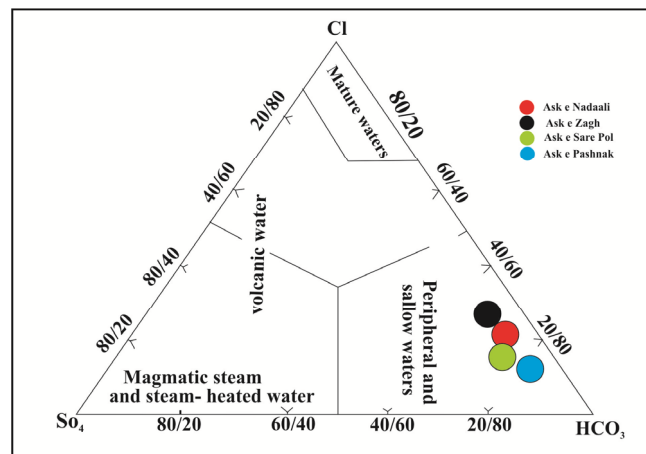


Figure 16. Triangular plot of Cl-HCO₃-SO₄ for the separation of volcanic water from magmatic vapors, mature water and shallow water (Giggenbach, 1991).

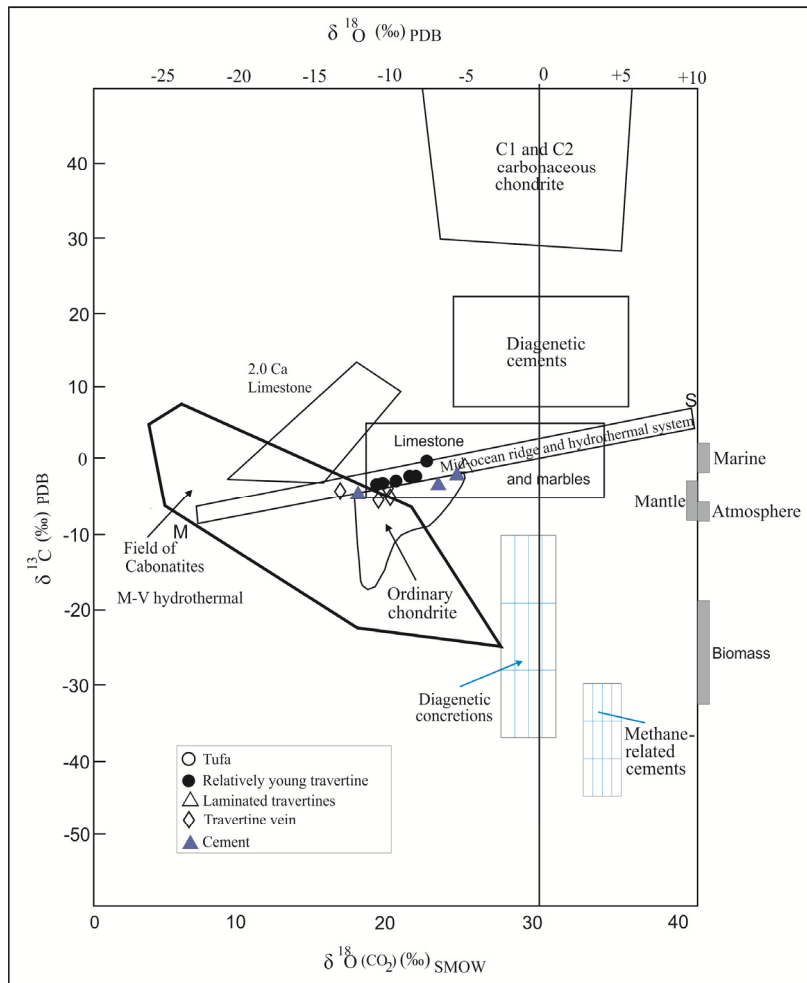


Figure 17. $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$ chart, carbonate ranges of different origins (Rollinson, 1993). The samples are in the hydrothermal fluid range.

The presence of algae in the studied travertine samples was confirmed in images taken with the scanning electron microscope (SEM). Plants often play a significant role in the formation of different types of travertine, especially in surface deposits. In addition, using SEM images, existence of single-cell algae such as diatoms have been proven in the studied samples. How the travertines are enriched with ^{13}C can be explained as follows: algae are spread over the surface of travertine deposits and, use carbon dioxide with light carbon isotope (^{12}C) to produce organic materials for their soft tissues by performing photosynthesis, eventually the carbon dioxide remaining in the water is enriched with heavy carbon isotope (^{13}C) and the travertine from this water is enriched. The skeleton of plant microorganisms, such as algae, helps the deposition of calcium carbonate during breathing and photosynthesis.

Discussion

Examining isotope data shows that the travertines become relatively enriched with $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ by getting away from the springs, so that those travertines near the outlets of springs have $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of about +6 and -13 per mils, and by getting away from the springs, they reach the values of about 9.8 and 9.3 per mils according to the VPDB standard (Table 2). There is linear relationship between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the Ab-e Ask travertines (Fig. 19A, 19B). This isotopic linear trend may have been due to several reasons, such as: 1) fluid mixture with different isotope compositions of carbon and oxygen such as water reacting with calcareous reservoirs, hydrothermal water and highly superficial meteoric water, 2) long-term variations of temperature, 3) diagenetic alteration through meteoric fluids, and 4) a combination of these factors (Guidry & Chafetz, 2002).

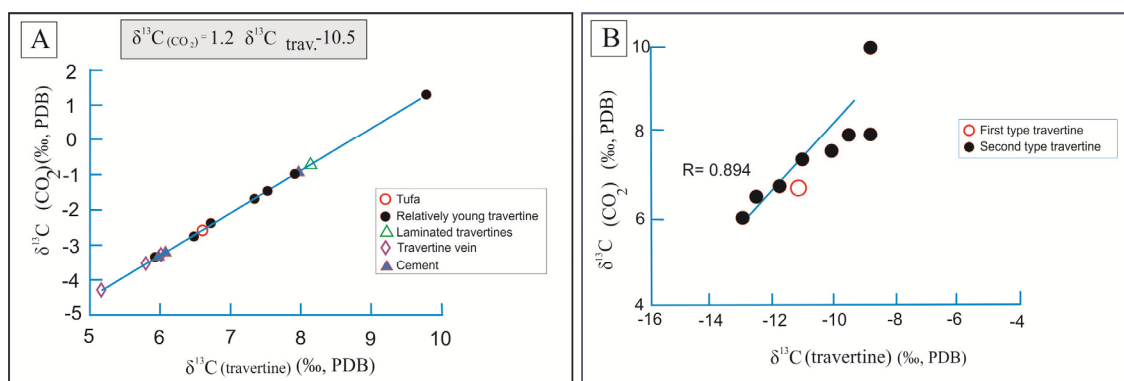


Figure 18.(A) Linear trend observed in oxygen and carbon isotope values chart plotted for the studied samples; (B) $\delta^{13}\text{C}(\text{CO}_2) - \delta^{13}\text{C}$ chart of travertine.

Regarding the linear trend observed between carbon and oxygen isotopes carbonate deposits show enrichment in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. Carbonate rocks, which are subject to contact metamorphism, are decarbonated and result in ^{13}C -rich travertine (Turi, 1986). This reason was noted for the ^{13}C -rich travertines throughout Italy. Kele *et al.*, (2011) attributed the enrichment of travertines in the Pamukkale region in terms of $\delta^{13}\text{C}$ to CO_2 released by thermo metamorphism reactions, so it is likely that the enrichment of the studied travertines in terms of $\delta^{13}\text{C}$ values is due to the reaction of heavy CO_2 (rich in ^{13}C) in the thermo metamorphic dissolution of host carbonate rocks (Mesozoic limestone) (Liu *et al.*, 2003; Pentecost, 2005). Studies show that the ^{13}C values in the water-calcite system are largely regulated by isotope fractionation processes during carbon dioxide-supersaturated mineral-water degasification. Degasification has a great impact on the carbon isotope composition due to the loss of light carbon (^{12}C). As a result, the carbon remained in the solution is enriched with ^{13}C . The rate of degasification and deposition of hot water is fast if the stable carbon isotope composition is high, and enrichment of ^{13}C often reflects the heavier carbon released due to the decomposition of marine limestone (Pentecost and Viles, 1994). The $\delta^{18}\text{O}$ values of travertines in the studied region also increase by getting away from the springs; in other words, specimens located near the springs have lower $\delta^{18}\text{O}$ values. Low quantities of oxygen isotope show that these travertines are deposited from high-temperature fluids. On the other hand, the passage of time and the decreased temperature of the fluid during deposition are considered as the most important factors controlling isotope changes and the enrichment of travertines with $\delta^{18}\text{O}$ (Lohmann,

1988).

Conclusion

The Ab-e Ask region is located in an active tectonic zone, and this area has become a permeable region since it is influenced by several faults and over thrusts. This has led to the formation of channels within the rocks and formations of the region, and consequently, atmospheric water containing a large amount of carbon dioxide can easily penetrate. The penetration of atmospheric waters, with high acidity, has led to the dissolution of carbonate rocks, and eventually appeared as calcareous springs on the ground and formed the abundance of travertine deposits. Based on $\delta^{18}\text{O}$ values and $\delta^{13}\text{C}$ of the original CO_2 calculated, it seems that these travertines were deposited from hydrothermal metasomatic fluids.

Different types of travertines in the Ab-e Ask region include cascade, fissure-ridge, hill and flow travertines. Calcium carbonate intended for the activity of travertine deposit spring and formation of travertine deposits in the region has been provided by dissolution of the limes belonging to the region's second and third periods.

According to the results of petrographic studies and XRD analysis, the mineralogical composition of travertines in the Ab-e Ask region consists of about %95 calcite and a small amount of quartz with biological origin. The algae strands in thin section and results of SEM analysis show that some of them formed by calcite with block texture. Changing discharge regime, may have been seasonal, has changed the amount of colored material, thereby the formation of multiple layers with different colors in travertine. The water of these springs is of calcium bicarbonate type with less or more acidic pH (6) and contains H_2S and

CO₂. According to the isotope analyses carried out on carbonate deposits and the linear trend between observed between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, these springs may have been mixed with different sources of fluids. Also, isotope-geochemical studies show that the latent source of magmatic activities in the region has also played a role in the occurrence and emergence of these springs. The results of isotope studies indicate that the CO₂ existing in the Ab-e Ask calcareous springs has two marine and mantle sources. Also, the emergence of springs in two environments containing Mesozoic and Cenozoic

lime formations and in the lavas of Damavand Peak indicates the impact of country rock on water. The source of water of the Ab-e Ask springs shows the effect of both atmospheric water and the water with deep and volcanic origin using the isotope-geochemical data.

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References

- Al-Kohlani, T.A.M., 2008. Geochemistry of thermal waters from the Al-Lisi – Isbil geothermal field, Dhamar governorate, Yemen. Report, 10: 53-76.
- Allenbach, P., R. Shteyger, 1966. Geologic map of Damavand 1:100000 survey sheet. – Geological Survey of Iran.
- Altunel, E., Hancock, P. L., 1993a. Morphology and structural setting of Quaternary travertines at Pamukkale, Turkey. Geological Journal, 28: 335 - 346.
- Ansari, M.R., 2013. Hydrochemistry of the Damavand Thermal springs, North of Iran. Life Science Journal, 10:866-873.
- Atabey, E., 2002. The formation of fissure ridge type laminated travertine-tufa deposits microscopical characteristics and diagenesis, Kiersehir Central Anatolia. Mineral Research and Exploration Bulletin, 123-124:59-65.
- Bargar, K. E., 1978. Geology and thermal history of Mammoth hot springs. Yellowstone National
- Brogi, A., Capezzuoli, E., 2009. Travertine deposition and faulting: the fault-related travertine fissure ridge at Terme S. Giovanni, Rapolano Terme (Italy). International Journal of Earth Sciences (Geol Rundsch), 98: 931-947.
- Burnside, N.M., 2010. U-Th dating of travertines on the Colorado Plateau: implications for the leakage of geologically stored CO₂. Ph.D thesis, University of Glasgow.
- Chafetz, H.S., Folk, R.L., 1984. Travertines: depositional morphology and the bacterially constructed constituents. Journal of Sedimentary Petrology, 54: 289-316.
- Chafetz, H.S. Guidry, S.A., 1999. Bacterial shrubs Crystal shrubs and ray-crystal crust bacterially induced vs. abiotic mineral precipitation. Sedimentary Geology, 126: 57-74.
- Ehteshami-Moinabadi, M., Nasiri, S., Geometrical and structural setting of landslide dams of the Central Alborz: a link between earthquakes and landslide damming. Bulletin of Engineering Geology and Environment. (2017), doi: 10.1007/s10064-017-1021-8
- Emami, M.H., Babakhani, A., 1997. Geological map of Damavand. Scale 1:100,000. Geological Survey of Iran, Tehran.
- Ferreri, V., 1985. Criteri di analisi di facies e classificazione dei travertine pleistocenici dell'Italia meridionale. – Rend. Acc. Scienze. Fis. e Mat. (Napoli), 52: 1-47.
- Ford, T.D., Pedley, H.M., 1996. A review of tuff and travertine deposits of the world. Earth Science Review, 41:117-175.
- Giggenbach, W.F., 1991. Chemical techniques in geothermal exploration. Application of Geochemistry in Geothermal Reservoir Development (Co-ordinator D'Amore, F). UNITAR/UNDP Centre on Small Energy Resources, Rome, 119-144.
- Guidry, S.A., Chafetz, H.S., 2002. Petrography and stable isotopic trend associated with Mammoth hot spring travertine, Yellowstone National Park, Wyoming. 33rd Annual Lunar and Planetary Science Conference, Houston, Texas, abstract no.1149.
- Hancock, P.L., Chalmers, R.M.L., Altunel, E., Cakir, Z., 1999. Travertines: using travertines in active fault studies. Journal of Structural Geology, 21: 903-916.
- Janssen, A. Swennen, R. Podoor, N., Keppens, E., 1999. Biological and diagenetic influence in recent and fossil tufa deposits from Belgium. Sedimentary Geology, 126:75-95.
- Jones, B., Renaut, R.W., 2010. Calcareous Spring Deposits in Continental Settings. In: Alonso-Zarza, A.M., Tarnner, L.H. (Eds), Carbonates in Continental settings. Facies, Environments and Processes. Elsevier, Amsterdam, pp. 177-224.
- Kele, S., Demeny, A., Siklosy, Z., Nemeth, T., Maria, T., Kovacs, M.B., 2008. Chemical and stable isotope compositions of recent hot-water travertines and associated thermal waters, from Egerszalók, Hungary: depositional facies and non-equilibrium fractionations. Sedimentary Geology, 211: 53-72.
- Kele, S., Özkul, M., Forizs, I., Gökgöz, A., Baykara, M.O., Alçiçek, M.C., Nemeth, T., 2011. Stable isotope geochemical

- study of Pamukkale travertines: New evidences of low-temperature non-equilibrium calcite-water fractionation. *Sedimentary Geology*, 238(1): 191-212.
- Kitano, Y. 1963. Geochemistry of calcareous deposits found in hot springs. *Journal of earth sciences, Nagoya University* 11:68-100
- Koban, C. G, Schweigert G., 1993. Microbial origin of Teravertine fabrics. Two examples from southern Germany (Pleistocene Stuttgart Teravertines and Miocene Riedoschingr Teravertine). *Facies*, 29: 251-264
- Liu, Z., Zhang, M., Li, Q., You, S., 2003. Hydrochemical and isotope characteristics of springwater and travertine in the Baishuitai area (SW China) and their meaning for paleoenvironmental reconstruction. *Environmental Geology*, 44: 698–704.
- Lohmann, K.C., 1988. Application of carbon and oxygen isotopic techniques for unraveling the diagenetic history of carbonate sequences. in Allan, J. R. and Harris, P. M., eds., *Stable isotope, trace element, and fluid inclusion workshop*, Chevron Oil field research Co., unpublished report, 1-49.
- Panichi, C., Tongiorgi, E., 1976. Carbon isotopic composition of CO₂ from springs, fumaroles, mofettes and travertines of central and southern Italy: a preliminary prospection method of geothermal area, Proc. 2nd UN Symp. on the Develop. and Use of Geotherm. Energy, 20–29 May 1975, San Francisco, U.S.A, 815–825.
- Pedley, H.M., 1990. Classification and environmental models of cool freshwater tufas. *Sedimentary Geology*, 68: 143–154.
- Pedley, M., 2009. Tufas and travertines of the Mediterranean region: a testing ground for freshwater carbonate concepts and developments. *Sedimentology*, 56(1): 221-246.
- Pentecost, A., 1995b. The microbial ecology of some Italian hot-spring travertines. *Microbios*, 81: 45–58.
- Pentecost, A., 1995a. The Quaternary travertine deposits of Europe and Asia Minor. *Quaternary Science Reviews*, 14: 1005–1028.
- Pentecost, A., 2005. *Travertine*. Springer-Verlage, Berline Heidelberg, Netherland, 445 pp.
- Pentecost, A., Viles, H., 1994. A review and reassessment of travertine classification. *Geographie physique et Quaternarie*, 48:305–314.
- Piper A.M., 1944. A graphic procedure in the geochemical interpretation of water analysis. *Trans. American Geophysical Union* 25 (6): 914-928.
- Rahmani Javanmard, S., Faramarz Tutti, T., Omidian, S., Ranjbaran, M., 2012. Mineralogy and stable isotope geochemistry of the Ab Ask travertines in Damavand geothermal field, Northeast Tehran, Iran. *Central European Geology*, 55(2): 187–212.
- Rahmani Javanmard, S., Tutti, F., Omidian, S., Ranjbaran, M., 2012. Mineralogy and stable isotope geochemistry of the Ab Ask travertines in Damavand geothermal field, Northeast Tehran, Iran. *Central European Geology*, 55: 187-212.
- Rollinson, H.R., 1993. *Using Geochemical Data*, Longman Scientific and Technical, 420.
- Stack, D.S., O'Neil, J.R., 1982. Mineralogy and stable isotope geochemistry of hydrothermally altered oceanic rocks. *Earth and Planetary Science Letters*, 57: 258-304.
- Turi, B., 1986. Stable isotope geochemistry of travertines. in: Fritz, P., Fontes, J.Ch. (Eds.), *Handbook of Environmental Isotope Geochemistry*, 2. Elsevier, Amsterdam, 207–238.
- Uysal, T., Feng, Y., Zhao, J., Isik, V., Nuriel, P., Golding, S.D., 2009. Hydrothermal CO₂ degassing in seismically active zones during the late Quaternary: *Chemical Geology*, 265: 442-454.