Sedimentology and hydro-geochemistry of Garab travertines in southeast of Mashhad, Iran

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Abstract
Travertine deposits are a kind of continental carbonates that form in specific chemical, physical and biological conditions. Garab travertines in southeast of Mashhad are studied based on field, geochemistry (elemental and stable isotope analysis) and hydro-geochemistry analysis. Field and petrographic characterization led to recognize of crystalline crust, raft, foam, shrub, laminated, black mud and tufa lithofacies. These lithofacies are composed of calcite and aragonite mineralogy. They have high concentrations of Ca, Mg, S, Fe, Na and Sr and low concentration of Mn, P and Si. These lithofacies are enriched with respect to $\delta^{13}C$ and depleted with respect to $\delta^{18}O$ that can be related to algal origin and meteoric water, respectively. The type of Garab springs water is Ca- HCO_3^- - SO_4^{2-} and Na- Cl. This water is saturated with respect to bicarbonate and sulfate. The water composition and dissolved ions have a close relation to geological units (carbonate and evaporite) in Garab area.

Keywords: *Travertine, Lithofacies, Carbonates, Garab.*

Introduction

Travertine and tufa are freshwater continental carbonates (Asta *et al.,* 2017), which precipitate from cold and hot waters (Capezzuoli *et al.,* 2014) in lake, river and cave environments. Their deposits are one of the best evidence to interpret the paleoenvironment conditions (Kele *et al.,* 2011; Osácar *et al.,* 2013; Wang *et al.,* 2014). Some factors include organic (such as photosynthesis) and inorganic (such as ion exchange, solution and weathering) as well as evaporation processes lead to CO_2 outgassing, fluid saturation and rapid deposition of these types of carbonates (Kanellopoulos, 2012; Ascione *et al.,* 2014; Kanellopoulos *et al.,* 2016). The travertine morphology can be affect by spring situation, form of initial cone and their substrate, chemical composition of springs and surface waters (Ozkul *et al.,* 2002). Travertine deposits mainly derived from hot springs with high concentrations of dissolved calcium and bicarbonate waters (Alonso- Zarza & Tanner, 2010). Travertine depositional zones are mostly affected by active faults and extensional forces that can create fractures and joints which groundwater can move upward and finally appear on surface in the form of hot springs. Some researchers (e. g. Hancook *et al.,* 1999) use travertonic for travertine zone with tectonic activity. The Garab travertine deposits in Binaloud zone are one of the recent carbonate deposits in southeast of Mashhad. The purposes of this study are: 1) to recognize various types of lithofacies based on field and microscopic observations (active and inactive forms), 2) to interpret the mechanism of formation, 3) to identify the hydrochemistry of spring's water and 4) the relationship between hydrochemistry and lithofacies formation with water flow.

Geological setting

The Garab travertines (Quaternary to recent) are located about 49 km southeast of Mashhad along the old Mashhad- Neyshbur road, between Binaloud mountains and Mashhad plain (35° 59′ 14.9″ N and 59° 38′ 12.1″ E) (Fig.1). The Binaloud zone is composed of Paleo- Tethys remnants including diorite, meta- flysch, meta- ophiolite and granodiorite (Karimpour *et al.,* 2010). Based on Fariman Geological map (Haddadan, 2008), this area contain limestone, marl and evaporate units that is covered by Neogen sediments. Presence of many fractures and joints are related to acting extensional fault systems of Sangbast- Shandiz in southeast of Grab area (Zeraatkar & Rahimi, 2012) that led to discharge of groundwater as hot springs. These fractures are visible that caused to breaking travertines structures to smaller sheets on spring cone surface. All of these evidences confirmed the active tectonics in Garab area before and after formation of travertine deposits (Zeraatkar & Rahimi, 2012). The height and width of the main cone is 18 and 4 m respectively, that located on a hill with a height of 30 m (Fig. 2). Evidence of CO_2 outgassing in springs can be seen by bubbles exist where travertine precipitation is continued to present day. The old (inactive) and recent (active) travertines are deposited between Neogene red marls as six small cascading systems. The distance of these springs about 500 m from each other. These systems have cone nozzles with different sizes.

Material and methods

During the fieldworks at Garab area we collected 30 samples of different travertine lithofacies from different subenvironments.

These samples are collected from surrounding springs, ponds and waterfall walls and classified based on Pentecost & Viles (1994). Two rock samples selected for mineralogical study by X- ray diffraction (XRD) method with EXPLORER TCU 2000N machine. In XRD method, 2 circle samples prepared with 1.5 centimeter diameter.

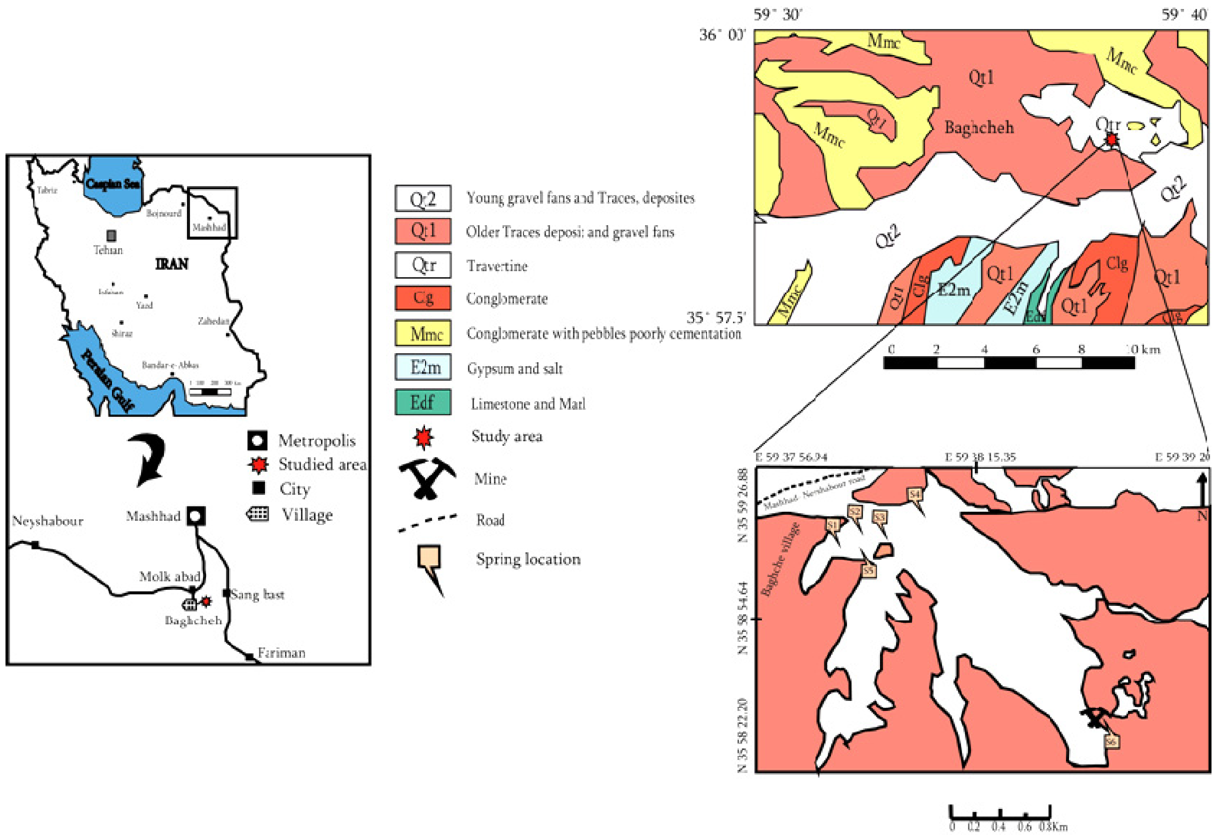

Figure 1. Part of Geological Map of Fariman (1:100000) area (Modified after Haddadan, 2008) that show the study area.

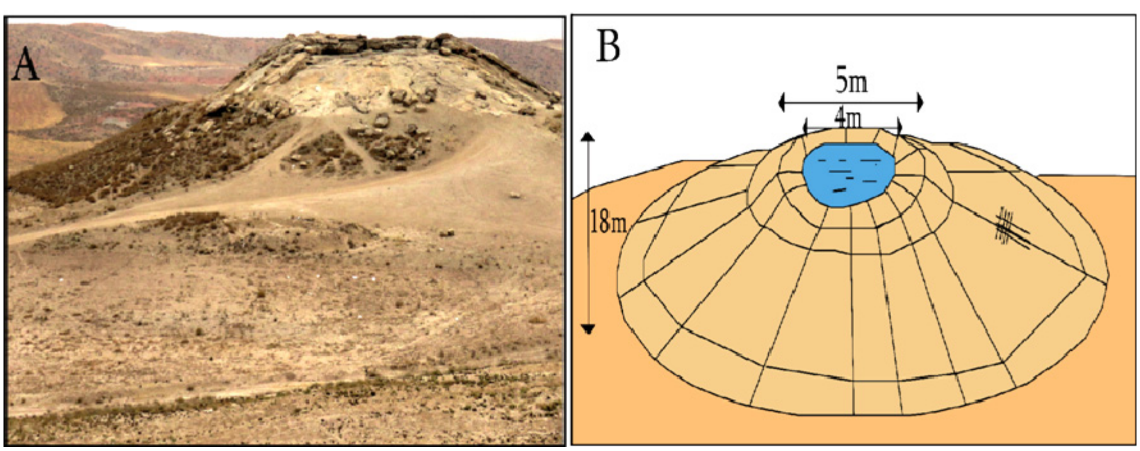

Figure 2. Field photo of the details of main Garab spring on volcano mound (A) and schematic figure of it (B).

Six samples also selected from microstructure and crystalline forms for SEM study. The machine is LEO 1450VP. These samples prepared in 1×1 centimeter dimension and are coated by gold. Five powder samples of lithofacies also prepared for major and trace elemental analyses with SPECTRO ARCOS System. The results of elemental analysis are shown in Table 1. All these analyses were done in Central Laboratory of the Ferdowsi University of Mashhad. For stable isotope analysis, 2 grams from 6 powder samples are prepared using dental drill in Sedimentology Lab and sent to the Hatch Stable Isotope Laboratory at the University of Ottawa- Canada.

Six water samples collected during field work and their locations are shown in Table 2. These samples collected from 30 centimeters depth within 100 ml bottles (washed with distilled water in three steps). They are analyzed for measurement of the main dissolved cations and anions (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) using atomic absorption (670 Shimadzu model) and (HCO_3^-, SO_4^{2-}, Cl^-, NH_3^-) using titration method in Geochemistry Lab of the Ferdowsi University of Mashhad. The pH and EC of water samples are measured 48 hours after sampling in the lab (these samples were kept in dark environments at 4°C). The types of water at Garab springs are also classified using Piper diagram (Piper, 1944) and the origin of dissolved ions are determined by compound diagrams.

Results

Lithofacies

Based on field and laboratory characterization (Goleij *et al.,* 2017a), seven lithofacies are recognized in Garab travertines with different morphology. They include crystalline crust, raft, foam, shrub, laminated, black mud and tufa lithofacies and are described below:

Crystalline crust lithofacies: This lithofacies with botryoidal shape consists of several dense layers with various colors such as white, cream to brownish (Fig. 3 A, B).

The maximum thickness alternation of dark and light laminations are 4.5cm that formed on the surfaces of laminated and porous travertine. Petrographic studies show alternation of dark and light lamina with various thicknesses and wavy forms (Fig. 3 C, D and E). The spary calcite crystals have radial fabric.

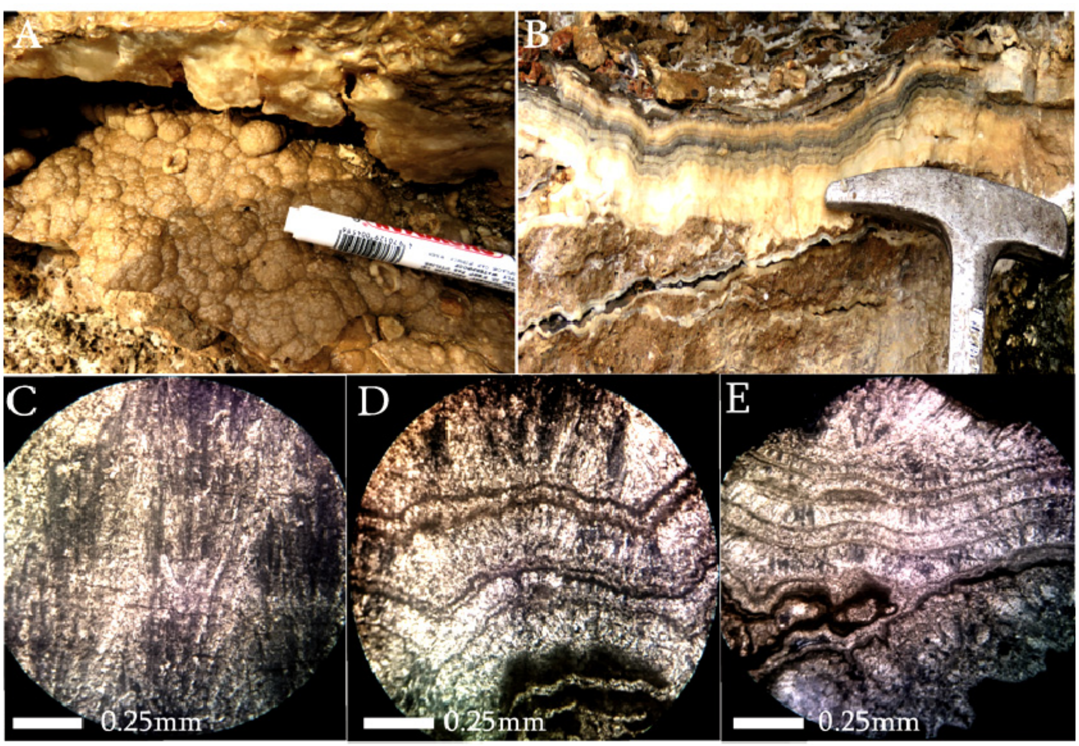

Figure 3. Field and microscopic photos of crystalline crust lithofacies. A) Botryoidal shape. B) Various lamina in different color. C) The radial form of botryoidal shapes in microscopic scale. D) Dark and light lamina with sub parallel shape. E) Wavy form lamination.

Similar lithofacies are found in Euboea Island in Greece (Kanellopoulus, 2012), Italy (Gandin & Capezzuoli, 2014), Denizli basin in Turkey (Ozkul *et al.,* 2002) and Badab- e Surt and east Azerbaijan basin in Iran (Sotohian & Ranjbaran, 2015; Zarasvandi *et al.,* in press).

Raft travertine lithofacies: This lithofacies is white, cream to brownish in color with uncondensed structures (Fig.4. A). The rafts thickness is approximately 2mm and made of a micritic lamina with microbial origin.

The general form of this lithofacies is a single raft that broken to oval form pieces. This lithofacies was called ice calcite by Weed (1889) and hot water ice by Allen & Day (1935) (Fig. 4. B). Similar lithofacies formed in Mammoth hot springs and Yellowstone National Park in USA (Fouke *et al.,* 2000), Denizli basin in Turkey (Ozkul *et al.,* 2002), Euboea Island in Greece (Kanellopoulus, 2012) and Italy (Gandin & Capezzuoli, 2014).

Foam travertine lithofacies: This lithofacies is formed as spherical bubbles that covered the drowned pool pebbles. These bubbles have 1-2 mm in diameter. The structures of the foam lithofacies consist of elongated tubes due to presence of elongated bubbles on the algal mats that covered the pebbles. Some of these forms in the upper parts have open pores due to increasing pressure for moving up the gasses and/or toward a place with low pressure (Fig. 5).

All the pores have a unique direction. Similar lithofacies are also formed in Mammoth hot springs and Yellowstone National Park in USA (Fouke *et al.,* 2000), Euboea Island in Greece (Kanellopoulus, 2012) and Italy (Gandin & Capezzuoli, 2014).

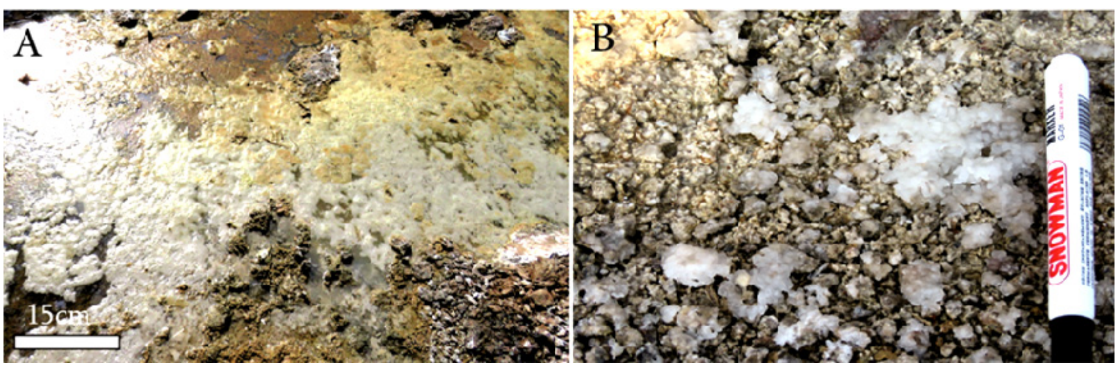

Figure 4. Field photos of raft travertine lithofacies. A) Raft carbonates on pool water surface. B) Ice calcite covered pebbles in margin pools.

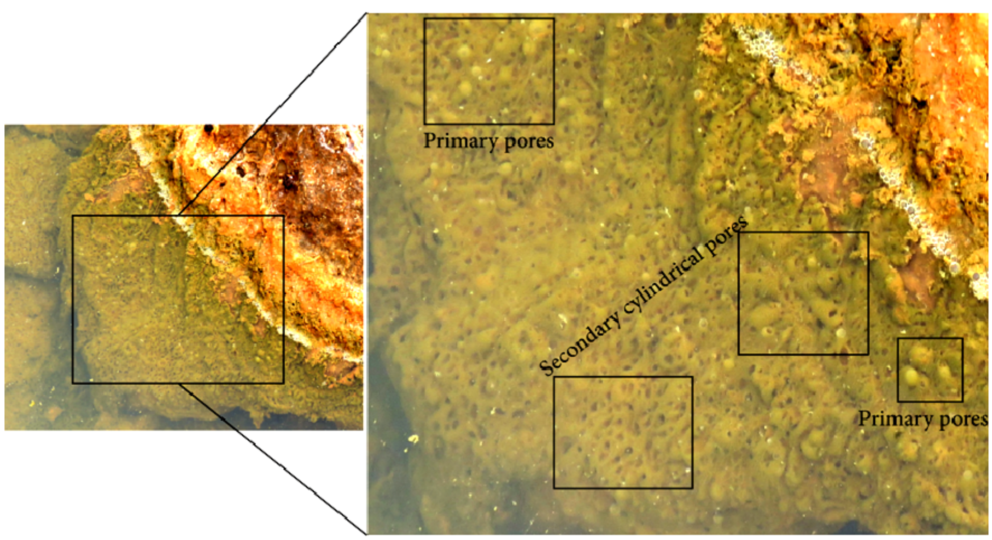

Figure 5. Foam lithofacies. Elongate tubes with unique directions and open pores.

Shrub lithofacies: This lithofacies with massive form has parallel lamination (bindstones). This type of travertine is formed with spary calcite and micrite lamina that are visible without microscope and is a few centimeters thick. The shrubs separated from each other with micrite lamina and grow up with regular geometrical forms (Fig. 6 A, B). This lithofacies is formed at the dried pools wall along the main Garab spring.

Similar lithofacies are formed in Mammoth hot springs and Yellowstone National Park in USA (Fouke *et al.,* 2000), Denizli basin and Pamukkale in Turkey (Ozkul *et al.,* 2002), Euboea Island in Greece (Kanellopoulus, 2012) and Italy (Gandin & Capezzuoli, 2014).

Laminated lithofacies: Lamination is a common form in Garab travertine deposits. This set is consisting of alternation of spary calcite and micrite with different colors such as orange, cream, white and gray based on water chemistry with maximum thickness of 2 cm. This lamination can be seen in microscopic and macroscopic scales in two wavy and parallel forms (Fig. 7 A-C). Dissolution features with micro and macro porosities as well as micro fractures are formed and filled by secondary calcite. The presence of micro porosity can be influenced by CO_2 outgassing. Similar lithofacies is formed in Euboea Island in Greece (Kanellopoulus, 2012).

Black mud lithofacies: This type of travertine is formed in the springs mound and within pools. The appearance of this lithofacies is muddy with a black color that is accompanied by knobby appearance in their neighboring (Fig. 8 A, B).It has a thin cover (2-3 cm) that located on algal mats in the springs mounds. This lithofacies in Garab area is an active type travertine.

Tufa lithofacies: Presence of some calcified tubes in travertine structures with high porosity show the presence of plant stems and branches, while the saturated fluids flow on live plants. These lithofacies are forming now and we can classify them into active lithofacies although there are some evidences of inactive deposits (Fig. 9 A, B).

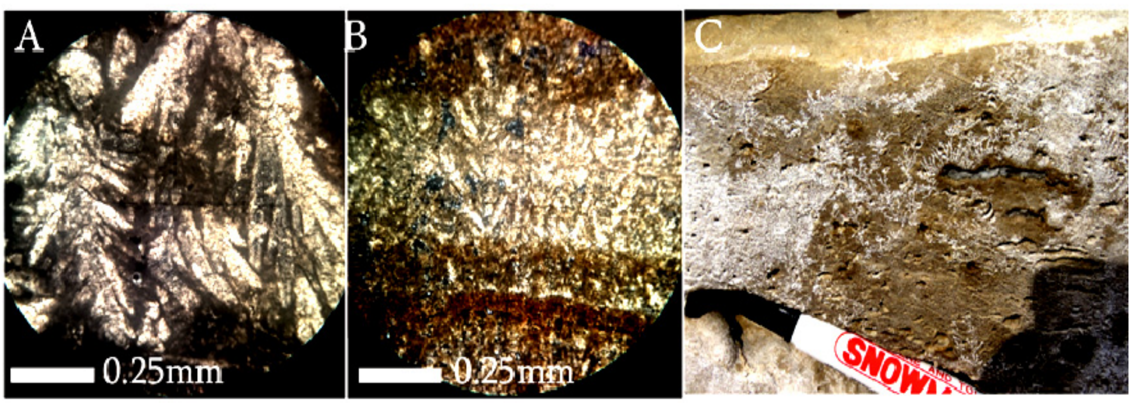

Figure 6. Microscopic and field photos of shrub lithofacies. A) Dendrites forms with upward growing. B) Shrubs forms with iron oxide margins. C) Dendrites prints affected by high evaporation in waterfall walls.

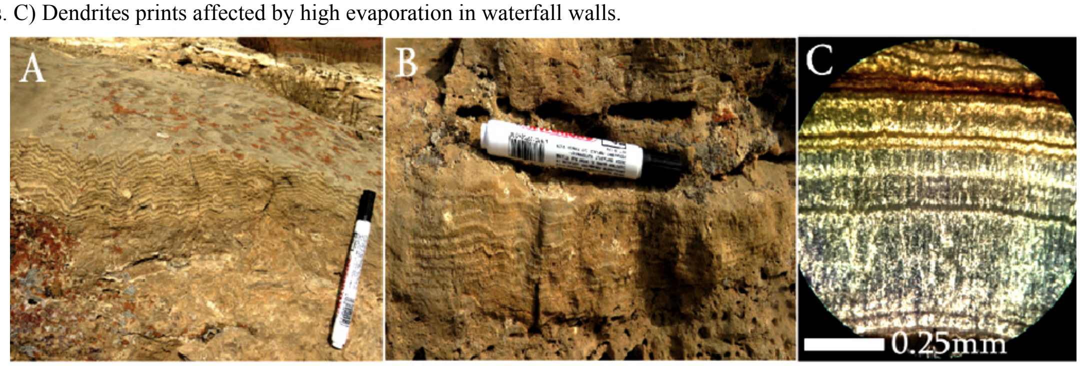

Figure 7. Laminated lithofacies. A) Field photo of wavy lamina with dark and light layers. B) Field photo of laminated lithofacies on porous travertine deposits. (C) Dark and light layers in microscopic view.

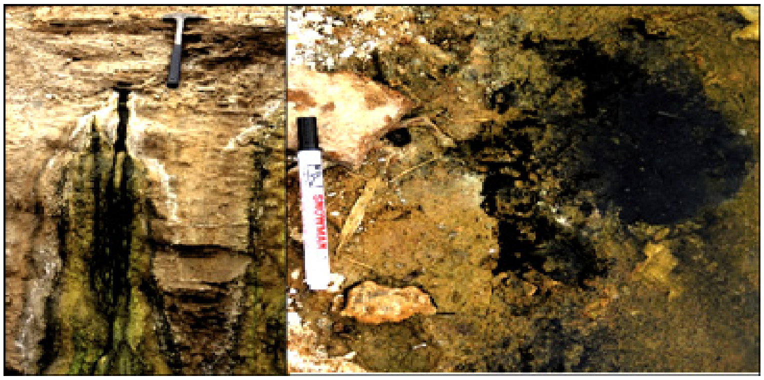

Figure 8. Field photos of black mud lithofacies in margin pools and cascades.

There are several layers on plant mold surface with cream color. This tufa is coated by crystalline crust lithofacies with small botryoidal shapes (Fig. 9 C). Tufa lithofacies have low frequently in Garab area and are similar with phytoherm framestone lithofacies in tufa deposits of Abgarm cascade in Kalat area (Goleij *et al.*, 2018).

Travertine mineralogy and geochemistry

Travertine lithofacies in Garab area are composed of calcite and aragonite minerals. Also cellulose, iron oxide (hematite), hydrogen sulfide and quartz as minor parts are present in these carbonate deposits (Fig. 10). Concentration of some elements in travertine deposits are shown in Table 1. Calcium is the highest content (37.7% to 28.88%), while Mg and Sr concentrations are 0.29 to 0.79% and 1.04 to 0.15%, respectively. These results (high concentration of Mg and Sr) can support the presents of aragonite mineralogy. The concentrations of S, Fe, Na are high while Mn and Si are low. Silica and Manganese concentrations range from 42.28 to 73.26 and 9.39 to 197.66 ppm, respectively.

Stable isotope analysis of Garab travertine lithofacies are provided in Table 2. They have high values of carbon isotope (8.02 to 13.42‰ VPDB) and -5.38 to - 7.79‰ VPDB for oxygen isotope. The highest value of carbon and oxygen isotope are related to crystalline crust lithofacies (13.42 to 7.79‰ VPDB). The different values of oxygen and carbon isotope can be related to precipitation of calcite and aragonite in different environments and under various conditions (Ozkul *et al.,* 2002).

Table 1. Element and stable isotope values of travertine lithofacies in Garab area.

Lithofacies.	Ca	Mg	S	Na	P	Sr	Fe	Si	Mn	$\delta^{18}O$	$\delta^{13}C$
%			ppm							‰VPDB	
Crystalline crust	32.51	0.79	2981.44	2903.53	36.67	10434.0	1419.49	55.43	39.82	-5.38	13.42
Crystalline crust	28.88	0.39	5484.44	3379.54	30.47	3142.30	91.21	45.03	9.39	-7.79	10.52
Laminated travertine	33.37	0.25	3541.40	469.24	68.74	2006.57	1147.50	73.26	110.6	-7.5	8.02
Raft travertine	37.07	0.58	4681.83	2440.53	43.25	5927.37	1418.43	64.15	89.78	-7.57	11.08
Laminated travertine	31.96	0.29	3732.73	3491.89	51.49	1520.99	2350.41	42.28	197.66	-7.1	8.73

Table 2. Location and chemical parameters of water samples in Garab area.

Spring No.	Location	pH	EC mS.cm^{-1}	TDS mg/L	Ca^{2+} ppm	Mg^{2+} ppm	HCO_3^- gr/ l	SO_4^{2-} gr/ l	Na^+ gr/ l	Cl^- ppm	K^+ ppm
1	N 35° 59′ 10.9″ E 59° 38′ 0.5″	6.4	15.8	10112	273.2	265.8	1.9	1.3	2.7	3	139.2
2	N 35° 59′ 9.7″ E 59° 38′ 4.2″	6.1	16	10240	443.5	123.2	1.8	1.1	2	2.7	127
3	N 35° 59′ 10.6″ E 59° 38′ 4.5″	6.6	16.8	10368	487.1	130.4	2	3.8	2.2	2.9	135.2
4	N 35° 59′ 2.5″ E 59° 37′ 54.6″	6.8	17	24832	495	125.6	1.7	1.3	2.2	3	139.2
5	N 35° 59′ 8.9″ E 59° 37′ 49.9″	6.7	16.4	12672	419.8	115.6	2	1.3	2	2.7	138.6
6	N 35° 59′ 14.9″ E 59° 38′ 12.1″	7	19.8	10880	332.6	106.3	2	1	2.8	3.5	216.8

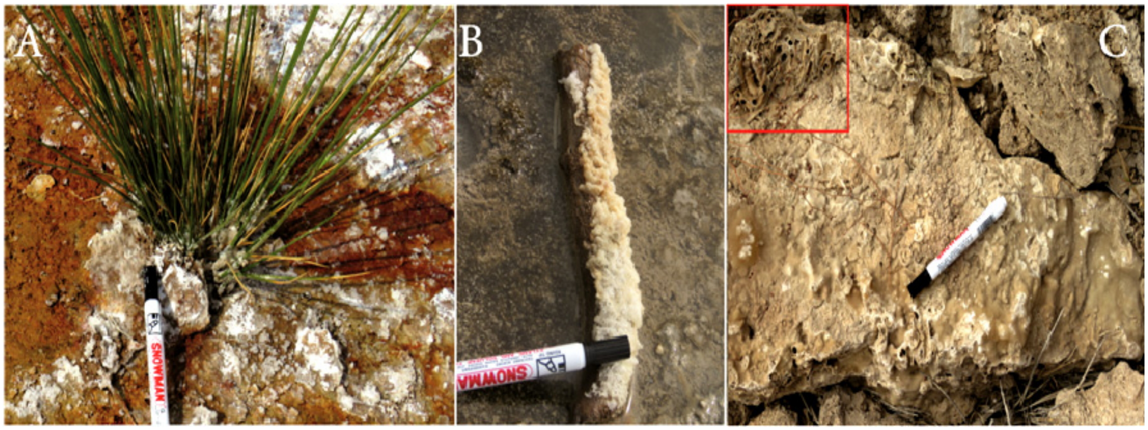

Figure 9. Field photos of tufa lithofacies. A) Active deposition on plant stems, B) Active deposition on broken branch. C) An inactive deposit with plant moulds remains.

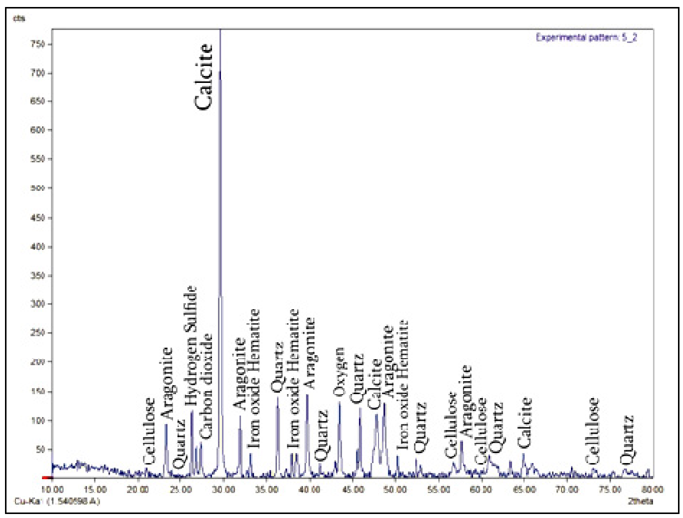

Figure 10. XRD analysis of crystalline crust lithofacies in Garab area.

Hydrochemistry

The hydrochemical analysis of Garab water samples are shown in Table 2. These springs are almost located close to each other with the relatively similar composition. The pH values range from 6.1 to 7 and the EC values from 15.8 to 17. As a general, the EC values have a direct relation with SO_4 and Cl concentrations as well as TDS content. The water samples that collected from springs systems show high concentration of HCO_3^-, Cl^-, Na^+, SO_4^{2-} and Ca^{2+} (1.42, 2.22, 1.73, 1.22 gr/l and 306.4 ppm).

These samples show saturation with respect to bicarbonate as the most important anions in freshwater (Nakhaei, 2012). In general all springs systems have the same concentrations of main anions and cations (Table 2) that could be related to their underground connection.

Discussion

Travertine forming mechanism

Garab area is an environment that appropriate for forming various lithofacies. Crystalline crust lithofacies can be precipitated directly from hot spring water with high flow rate (Alonso- Zarza & Tanner, 2010; Kanellopoulus, 2012) and on the inclined surface (Zarasvandi *et al.,* in press). At the first steps, this lithofacies is soft and uncondensed and gradually would be dense and rough by compaction (Alonso- Zarza & Tanner, 2010). The variety of colors can be related to water chemistry and concentration of dissolved ions such as iron (hematite). Recent surface water flow that saturated with respect to bicarbonate led to precipitation of new carbonate lamina.

In general, raft travertine can be formed in low energy ponds or in stagnant water (Ronchi, 2015). Decreasing wet conditions in upper parts, increasing turbulence by exiting high volume water and high wind blow on water surface caused to breaking these single and uncondensed sheets into smaller pieces (Gandin & Capezzuoli, 2014). As mentioned earlier, these structures consist of two upper and lower surfaces.

The upper part is smoother because of less contact with water and less wet conditions, while the lower part had suture forms due to continuing crystals growth. This growth caused to increases the weight and density of these sheets and at the next stage, they fall into the pools bottom. Repeating this process can form of these rafts on each other as condensed plate. Also water discharge caused to increase CO_2 outgassing and saturation with respect to bicarbonate and calcium that led to precipitation of these travertine sheets.

Based on Chafetz *et al.* (1991), the photosynthesis and oxygen outgassing caused to produce the bubbles that can see in algal mats margins, although these bubbles can be related to CO_2 outgassing from hot springs too. The other bubbles that formed in the primary stages have no hole on their upper surfaces. If there are no suitable conditions to preserve, the bubbles can be easily destroyed but if they could be lithified, the honeycomb or foam lithofacies will form (Jones & Renaut, 2010). Foam travertine lithofacies is a recent type (active) of travertine formation in Garab area that is not lithified yet.

The shrub lithofacies is a common part of trace pools (Guo & Ridding, 1994). This lithofacies is associated with laminated and raft travertine lithofacies. Based on Chafetz & Folk (1984) the shrubs are indicators of seasonal growth in spring and summer. The micritic laminas that separate these shrubs show stop in forming shrubs in winter season. The water temperature for the formation of shrubs should be higher than cool water springs (Ozkule *et al.,* 2002). Based on needle crystal of shrubs, the abiotic origin proposed for them (Pentecost, 1990).

The laminated lithofacies can be formed by inorganic as well as saturation fluids with respect to bicarbonate and sulfate anions. The irregular bands can be formed by deposition behind small dams in low- energy environments (Filipps *et al.,* 2013) and caused to create wavy laminated lithofacies. This structure is common on lake walls in main Garab cone on porous travertine surface with lichen covers.

The black mud lithofacies are formed in low flow energy, too. The high concentration of sulfur and their reaction with atmospheric oxygen caused to oxidize of these sulfur components and changed their color to dark and black (Figs. 8 A, B). The spring's water with this lithofacies has maximum contents of Cl, Na, HCO_3 and SO_4 and poor acidic conditions. These are very similar to lithofacies of Badab- e Surt in Mazandaran Province in north of Iran due to presence of high sulfur concentration (Sotohian & Ranjbaran, 2015).

Tufa lithofacies are forming in some places with plant cover and cooler water temperature respect to pools. The presence of this lithofacies is visible in lower parts of cascades. These environments are an appropriate place for plant growth even on the other lithofacies surface. These covers growth until all plant surfaces covered by carbonate deposits and avoiding of photosynthesis (Pedley *et al.,* 2003).

Geochemistry of Carbonates

The concentration of major and trace elements have a positive relation with fluid composition (Table 1). The concentration of Fe, Na, P and Si show presence of detrital particles in the form of quartz, plagioclase, sericite and microcline minerals that observed in thin sections too (Fig. 11).

The SEM shows trigonal calcite and cubic halite crystals in travertine lithofacies. (Fig. 12. A, B). These crystals are mainly filling the pore space in carbonate deposits. These results confirmed by EDS analysis that show high concentrations of Na and Cl and can be related to dissolution of evaporate units (Fig. 12. C).

High evaporation rate during warm and dry climate led to supersaturation of water with respect to Na and Cl. The low percentage of plants in travertine structures caused to a dense carbonate with low porosity (Pedley, 1990). Low presence of calcified plant stems in SEM in some parts of pore space deposits (Fig. 12. E) as well as in macroscopic calcified plant can be related to detrital tufa lithofacies. The rose shape crystals growth form toward bottom water surface. These crystals are filling pore space with halite crystals (Fig. 12. F).

High concentrations of Mg, Na, Cl and K in solids and water samples show high evaporation conditions that caused the high concentrations in the ponds fluid. Also low concentration of Si is due to less presence of siliciclastic particles.

The change of Mg content is related to temperature that effect in saturation and depositional rate (Tucker & Wright, 1990).

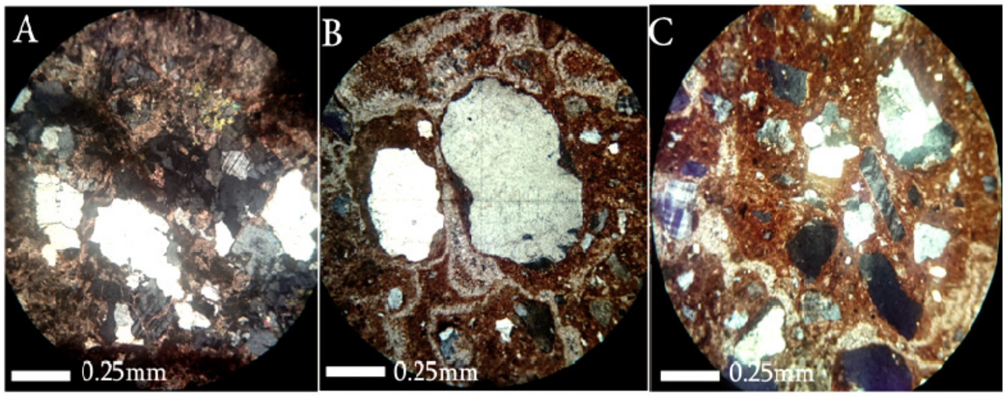

Figure 11. Microphotographs of detrital components in travertine deposits. A) Presence quartz, plagioclase and microcline in carbonate cement. B) Quartz and feldspars accompanied iron oxide. C) Frequently of quartz and microcline with iron oxide.

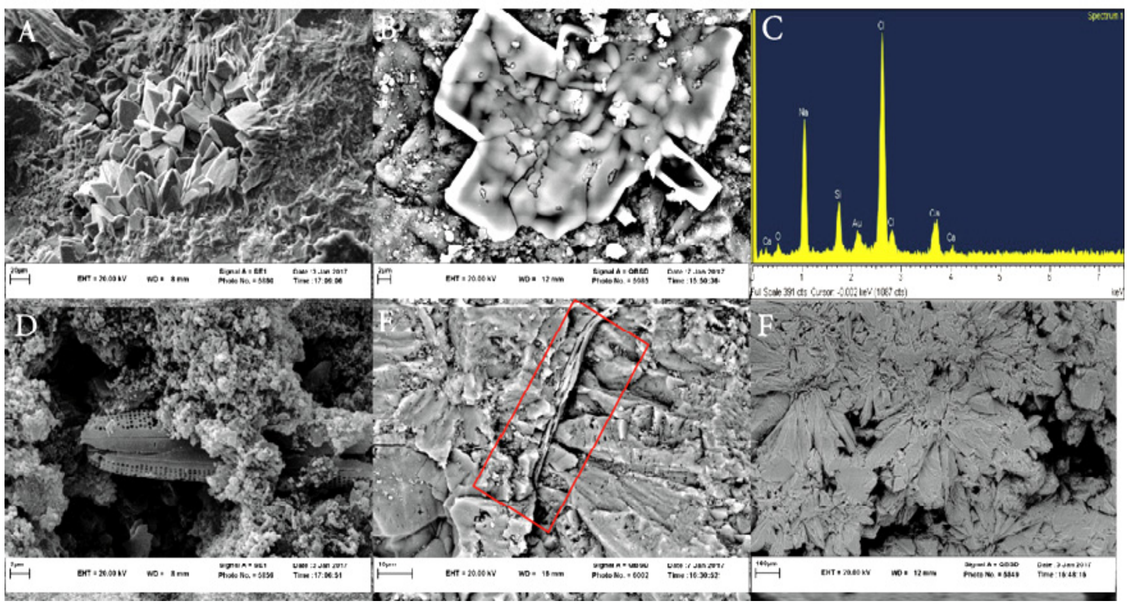

Figure 12. SEM photos. A) Trigonal calcite crystals. B) Cubic halite crystals in calcite. C) EDS analysis of cubic halite Rose form calcite. D) Diatom remains in calcite crystals. E) Plant remains in calcite ground. F) Rose form calcite in close view.

The affecting of various diagensis processes such as recrystallization and formation of calcite cements is accompanied by reduce in magnesium, strontium and zinc elements with increase iron element concentration (Pavlovic *et al.,* 2002).

High values of strontium can be related to bacterial activities that caused to replacement of strontium instead of magnesium in aragonite crystalline structure (Finch *et al.,* 2003).

Decreasing pressure and CO_2 outgassing occurred by going out of groundwater and flowing on the surface as hot springs. High water temperature and decreasing pressure caused the enrichment of carbon isotope enrichment. Stable isotopes analysis of Garab travertine lithofacies show high values of carbon isotope in range of 8.02 to 13.42‰ VPDB (with average of 10.35‰). The high values of stable carbon isotope are affected by CO_2 outgassing from the surficial run off and exiting water from the mouth of springs. $^{12}CO_2$ outgassing occurred due to gradual removing of pressure in upward moving and water discharge from the mouth of springs caused $\delta^{13}C$ enrichment in travertine facies. There is evidence of the presence of spindle shapes with regular structures of diatoms (Fig. 12 D). The $\delta^{18}O$ values range from -5.38 to -7.79‰ VPDB (with average of -7.06‰VPDB). These contents show depletion of $\delta^{18}O$ (Fig. 13) that can be related to high water temperature when these travertine lithofacies formed. Based on reported origin for $\delta^{18}O$ (Hoefs, 2015), these samples are in range of meteoric water with low contents of $\delta^{13}C$ and $\delta^{18}O$. Low periods contacts between meteoric water with travertine deposits through their porosities caused to chemical interaction between meteoric water and travertine lithofacies (Rahmani Javanmard *et al.,* 2012). So as clear, recent deposits have lower values of $\delta^{13}C$ and $\delta^{18}O$ due to lower contents of these stable isotopes for meteoric water. Gradually old travertine pore space, fractures and joints would be closed by acting diagensis process. These changes caused to decrease interaction between water and travertines by limited water movements (Fig. 13). In Figure 3, we compared $\delta^{13}C$ and $\delta^{18}O$ values of some travertine and tufa deposits in various places around the world. It shows the stable isotope values in Turkey and Italy are similar with Garab travertines and we can conclude that the formation conditions of studied area may have been similar to these locations.

Hydrochemistry

The water in Garab area is saturated with respect to Ca- SO_4, Na- Cl and Ca- HCO_3. This saturation is due to interaction between water and limestone, halite and gypsum units. The water type in warm water of Garab springs based on Piper diagram (Piper, 1944) is Ca- HCO_3- SO_4 and Na- Cl (Fig. 14).

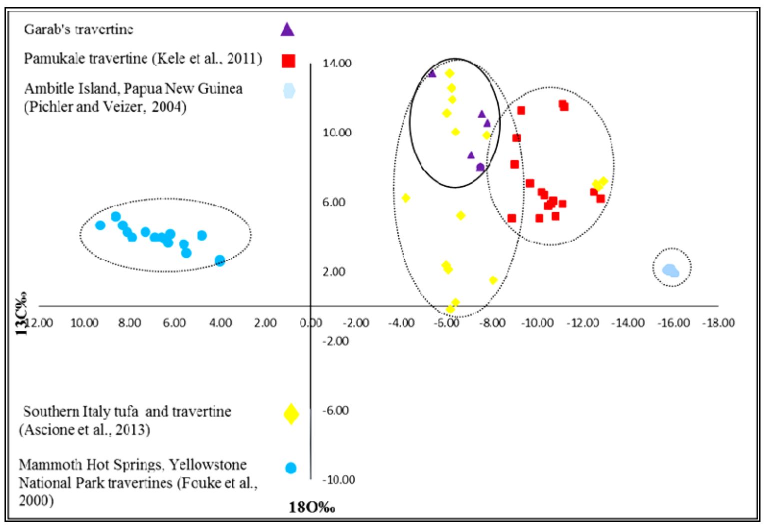

Figure 13. Scatter diagram of oxygen and carbon isotopes.

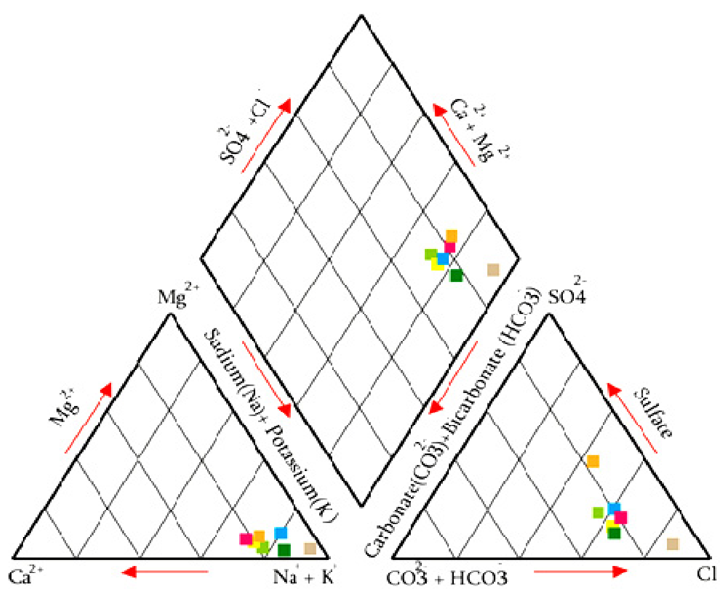

Figure 14. Piper diagram (Piper, 1944) of Garab springs water.

This result can be conformity by previous studied (Mansouri Daneshvar & Pourali, 2015). The calcium, magnesium, bicarbonate and sulfate concentrations show that these ions originate from dissolution of limestone and evaporate units (Dominguez- Villar *et al.,* 2017). The high concentration of Na is also can be related to salty units that can be more concentrate by evaporation in warm and dry seasons in this area. Presence of halite crystals in pore space of travertine is confirmed this interpretation.

Dissolution of evaporate units caused to create high concentrations of Na and Cl too. Based on total dissolved solids (TDS) in all springs water in Garab area, the type of water is brackish (saline range 1000- 10000 mg/r) (Nakhaei, 2012).

The similar concentrations of cations and anions in spring's water and the linear trend of some spring show that this water has an underground origin which is related to active tectonics in this region.

The component diagram of calcium and magnesium versus sulfate and bicarbonate show that each samples plotted below the equilibrium line (Fig. 15. A). This reveals dissolution of gypsum and cation exchange as well as carbonate dissolution in the subsurface water that have been done at the same time (Datta & Tyagi, 1996). The component diagram of calcium and magnesium versus bicarbonate show that most samples were plotted above the equilibrium line (Fig 15. B).

High concentration of calcium and magnesium can be related to dissolution of plagioclase and probably pyroxene minerals as well as limestone (Mohammadi & Kazemi, 2014).

The component diagram of Ca vs. SO_4^{2-} (Fig. 16 A) show that calcium concentration is higher than sulfate. It is due to increasing of weathering in calcite (Garrels & Mackenzie, 1971). Just one sample has higher concentration of sulfate than calcium that shows Ca may have been gradually removed from water due to calcite precipitation or increasing gypsum weathering. Also the (Ca^{2+} + Mg^{2+}) vs. (Cl^- + SO_4^{2-}) show the lower concentration of Cl^- and SO_4^{2-} in upper part of equation line that are related to siliciclastic minerals weathering and increasing calcium and magnesium concentrations in Grab waters (Mohammadi & Kazemi, 2014) (Fig. 16. B).

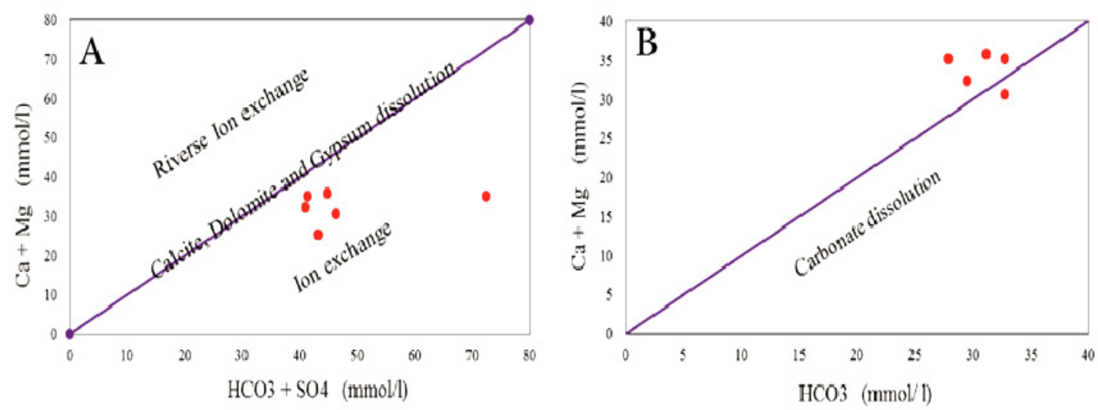

Figure 15. Component diagrams (Datta and Tyagi, 1996; Mohammadi and Kazemi, 2011). A) Ca and Mg vs. HCO_3. B) Ca and Mg vs. HCO_3 and SO_4.

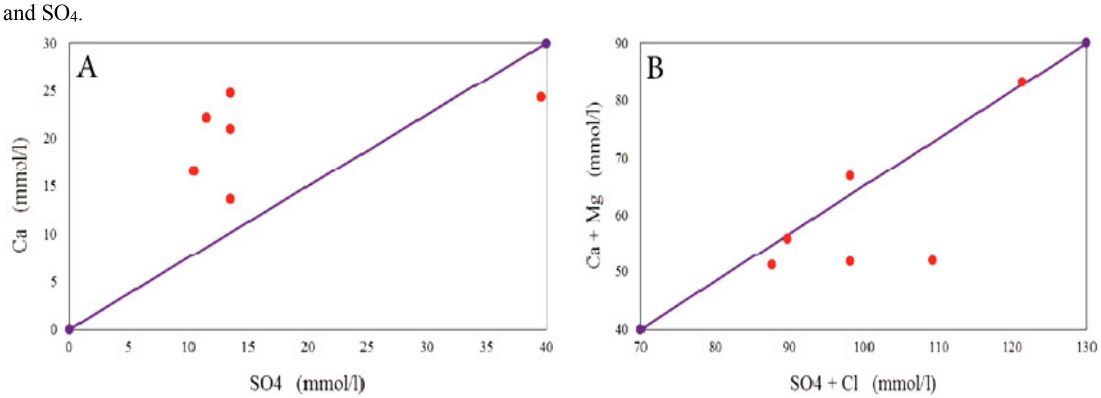

Figure 16. Component diagrams. A) HCO_3 Vs. sum anions. B) Ca vs. SO_4 (Hounslow, 1995; Garrels and Mackenzie, 1971).

Conclusion

The tectonically Garab area in southeast Mashhad is affected by extensional fault of Sangbast- Shandiz. This fault is the main reason for appearance of spring systems and formation of different travertine lithofacies such as crystalline crust, raft, foam, shrubs, laminated, black mud and tufa. Raft, foam, shrubs and black mud lithofacies are active deposits types in studied area. These carbonates have calcite and aragonite mineralogy with high concentrations of Ca, Mg, and Sr. Oxygen isotope compositions can be related to meteoric water while carbon isotope probably related to algal effects in the formation of travertine lithofacies that can be seen in active deposits. The type of Garab water springs is Ca- HCO_3- SO_4 and Na- Cl. This water has high concentrations of dissolved ions of bicarbonate, sulfate, sodium and calcium that are affected by interaction of water and rock. Dissolution of limestone, gypsum and saline layers release these ions. These ions are similar in each spring systems and are affected by active tectonic in Garab area. Tectonical origin of these springs confirmed by some liner springs along the direction in fault strike.

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References

Allen, E.T., Day, A.L., 1935. Hot springs of the Yellowstone National Park. Carnegie Institute of Washington Publication, Washington DC. 525pp.

Alonso- Zarza, A.M., Tanner, L.H., 2010. Carbonate in Continental Settings, Facies, Environments and Process, Elsevier. 378 pp.

Ascione, A., Lannace, A., Imbriale, P., Santangelo, N., Santo, A., 2014. Tufa and travertines of southern Italy: deep-seated, fault related CO_2 as the key control in precipitation. Terra Nova, 26: 1- 13.

Asta, M.P., Auque, L.F., Sanz, F. J., Gimeno, M. J., Acero, P., Blasco, M., Alix, A. G., Gomez, J., Huertas, A. D., Mandado, J., 2017. Travertines associated with the Alhama-Jaraba thermal waters (NE, Spain): Genesis and geochemistry. Sedimentary Geology, 347: 100- 116.

Capezzuoli, E., Gandin, A., Pedley, M., 2014. Decoding tufa and travertine (fresh water carbonates) in the sedimentary record: The state of the art. Sedimentology, 61: 1. 1–21.

Chafetz H.S., Folk R.L., 1984. Travertines: depositional morphology and their bacterially constructed constituents. Journal of Sedimentary Petrology, 54: 289–316.

Chafetz, H.S., Rush, P.R., Utech, N.M., 1991. Microenvironmental controls on mineralogy and habit of $CaCO_3$ precipitates: an example from active travertine system. Sedimentology, 38: 107–126.

Datta, P.S., Tyagi, S.K., 1996. Major ion chemistry of groundwater in Delhi area: Chemical weathering processes and groundwater regime. Journal of the Geological Society of India, 47: 179–188.

Domínguez□Villar, D., Vázquez□Navarro, J.A., Krklec, K., 2017. The role of gypsum and/or dolomite dissolution in tufa precipitation: lessons from the hydrochemistry of a carbonate–sulphate karst system. Earth Surface Processes and Landforms, 42(2): 245-258.

Filipps, L.D., Anzalone, E., Billi, A., Faccenna, C., Ponica, P.P., Sella, P., 2013. The origin and growth of a recently active fissure ridge travertine over a seismic fault, Tivoli, Italy. Geomorphology, 195: 13- 26.

Finch, A.A., Allison, N., Sutton, S.R., Newville, M., 2003. Strontium in coral aragonite: 1. Characterization of Sr coordination by extended absorption X-ray fine structure. Geochimica et Cosmochimica Acta, 67: 1189–1194.

Fouke, B. W., Farmer, J. D., Des Marais, D.J., Pratt, L., Sturchio, N.C., Burns, P.C., Discipulo, M.K., 2000. Depositional facies and aqueous- solid geochemistry of travertine- depositing hot springs (Angel terrace, Mammoth hot springs, Yellowstone national park, U.S.A.). Journal of Sedimentary Research, 70: 565- 585.

Gandin, A., Capezzuoli, E., 2014. Travertine: Distinctive depositional fabrics of carbonates from thermal spring systems. Sedimentology, 61: 264- 290.

Garrels R.M., Mackenzie F.T., 1971. Evolution of Sedimentary Rocks. 1st. Ed. Norton, New York, xvi, 397 pp.

Goleij, F., Mahboubi, A., Khanehbad, M. Moussavi- Harami, R., 2017a. Classification and formation mechanisms of travertine lithofacies of Garab area, NE Iran. 4th YES Congress. Geological Survey and Mineral Exploration of Iran, 120 -121.

Goleij, F., Mahboubi, A., Khanehbad, M., Moussavi- Harami, R., 2017b. Classification and formation mechanism of tufa facies of Abgarm area, NE Iran. Third Conference of Sedimentological Society of Iran, National Iranian Oil Company, Exploration Management, 484- 489 (in Persian with English abstract).

Goleij, F., Mahboubi, A., Khanehbad, M. Moussavi- Harami, R., 2018. Sedimentology and geochemistry of tufa and their relation to hydrochemistry of springs, an example of Abgarm Tufa of Kalat- east of Kopet- Dagh basin. Journal of Stratigraphy and Sedimentology Researches, University of Isfahan, 69(4):1- 20 (in Persian with English abstract).

Guo, L., Riding, R., 1998. Hot-spring travertine facies and sequences, Late Pleistocene, Rapolano Terme, Italy. Sedimentology, 45: 163–180.

Haddadan, M., 2008. Geological Map of Fariman Area (1: 100000) series, Fariman sheet, Geological survey of Iran.

Hancock, P.L, Chalmers, R.M.L., Altunel, E., Çakir, Z., 1999. Travitonics: using travertines in active fault studies, Journal of Structural Geology, 21(8–9): 903–916.

Hoefs, J., 2015. Stable Isotope Geochemistry. Springer –Verlag. 389 pp.

Hounslow, A.W., 1995. Water Quality Data: analysis and interpretation. CRC Press LLC, Florida. 416 pp.

Jones, B., Renaut, R.W., 2010. Calcareous spring deposits in continental settings. In: Continental Settings: Facies, Environments and Processes, (Eds. A.M. Alonso Zarza and L.H. Tanner), Elsevier, Amsterdam. 177–224.

Kanellopoulos, Ch., 2012. Distribution, lithotypes and mineralogical study of newly formed thermogenic travertines in Northern Euboea and Eastern Central Greece. Journal of Geosciences, 4: 545- 560.

Kanellopoulos, Ch., Lamprinou, V., Mitropoulos, P., Voudouris, P., 2016. Thermogenic travertine deposits in Thermopylae hot springs (Greece) in association with cyanobacteria microflora. Carbonates and Evaporates, 31(3): 239-248.

Karimpour, M.H., Stern, C.R., Farmer, G.L., 2010. Zircon U-Pb geochronology, Sr–Nd isotope analyses, and petrogenetic study of the Dehnow diorite and Kuhsangi granodiorite (Paleo– Tethys), NE Iran, Journal of Asian Earth Science, 37: 384–393.

Kele, S., Özkul, M., Gökgöz, A., Fórizs, I., Baykara, M.O., Alçiçek, M.C., Németh, T., 2011. Stable isotope geochemical study of Pamukkale travertines: new evidences of low temperature non-equilibrium calcite-water fractionation. Sedimentary Geology, 238: 191–212.

Mansori Daneshvar, M.R., Pourali, M., 2015. Hydrogeochemical and geomorphological investigation of travertine deposition in the Garab Spring region, NE Iran. Sustainability of Integrated Water Resources Management, 1: 253-262.

Mohammadi, A., Kazemi, Gh., 2014. Effect of geological formations on the groundwater quality in the aquifer of Shoghan plain aquifer (North Khorasan). Journal of Geosciences, Scientific Quarterly Journal, Published by Geological Survey of Iran, 90: 55-62 (in Persian with English abstract).

Nakhaei, M., 2012. Introduction to Groundwater. Arad book publication. 183 pp. (in Persian)

Osácar, C., Arenas, C., Vázquez-Urbez, M., Sancho, C., Auqué, L.F., Pardo, G., 2013. Environmental factors controlling the δ13C and δ18O variations of recent fluvial tufas: a 12- year record from the monasterio de piedra natural park (NE Iberian Peninsula). Journal of Sedimentary Research, 83(4): 309–322.

Özkul, M., Varol, B., Alçiçek, M.C., 2002. Depositional environments and petrography of Denizli travertines. Bulletin of the Mineral Research and Exploration, 125: 13–29.

Pavlovic, G., Prohic, E., Miko, S., Tibljas, Z., 2002. Geochemical and petrografic evidence of meteoric diagenesis in tufa deposits in northern Dalmatia (Zrmanja and Krupa rivers, Croatia). Facies, 46: 27- 34.

Pedley, H.M., 1990. Classification and environmental models of cool freshwater tufa. Sedimentary Geology, 68: 143–154.

Pedley, M., Martı ´n JAG, Ordo ´n ˇez SD, Garcı ´a Del Cura M.A., 2003. Sedimentology of quaternary perched springline and paludal tufas: criteria for recognition, with examples from Guadalajara Province, Spain. Sedimentology, 50: 23–44.

Pentecost, A., 1990. The formation of travertine shrubs: Mammoth Hot Spring, Wyoming: Geological Magazine, 127: 159-168.

Pentecost, A., Viles, H., 1994. A review and reassessment of travertine classification. Géographie physique et Quaternaire, 48(3): 305-314.

Pichler T, Veizer J. 2004. The precipitation of aragonite from shallow-water hydrothermal fluids in a coral reef, Tutum Bay, Ambitle Island, Papua New Guinea. Chemical Geology, 207: 31–45.

Piper, A.M., 1944. A graphical interpretation of water analysis. Transactions of the American Geophysical Union, 25(6): 914 -928.

Rahmani Javanmard, S., Toti, F., Omidian, S., Ranjbaran, M., 2012. Mineralogy and genesis of fissures hill and vein from Ab-e- Ask based on petrographic studies and carbon- oxygen isotope. Iranian Journal of Geology, 22: 51- 61. (in Persian with English abstract)

Ronchi, P., 2015. Continental carbonates as a hydrocarbon reservoir, an analog case study from the travertine of Saturnia, Italy. American Association of Petroleum Geologists Bulletin, 99(4): 711- 734.

Sotohian. F., Ranjbaran. M., 2015. Depositional system and facies analysis of travertine deposits: Badab-e Surt Spring Mazandaran, Iran. Arabian Journal of Geosciences, 8(7): 4939-4947.

Tucker, M., Wright, P., 1990. Carbonate Sedimentology. Blackwell Science, Oxford. 482 pp.

Wang, H., Yan, H., Liu, Z., 2014. Contrasts in variations of the carbon and oxygen isotopic composition of travertines formed in pools and a ramp stream at Huanglong Ravine, China: Implications for paleoclimatic interpretations. Geochimica et Cosmochimica Acta, 125: 34–48.

Weed, W.H., 1889. Formation of travertine and siliceous sinter by the vegetation of hot springs. Geological Survey of America. Annual Report, 9: 613–676.

Zarasvandi, A., Roshanak, A., Gratzer, R., Pourkaseb, H., Moore, F., In press. Stable isotope geochemistry of travertines from northern Urumieh-Dokhtar volcano-plutonic belt, Iran. Carbonates and Evaporates, 1-13.

Zeraatkar, K., Rahimi, B., 2012. Investigating the development of Sangbest-Shandiz fault zone and its geomorphological outcomes. Journal of Geography and Regional Development, 19: 196- 214.