Islamic Azad University
Mashhad Branch

Determination of Travertine Outcrop Types in Tazerj (Northern Hormozgan) using Mineralogical and Geochemical Data

Jamal Tarrah[1], Zahra Aedpour [2*], Seyed Mohammad Mirhosseini[3]

1 Islamic Azad University, Bandar Abbas Branch, Geology Department, Bandar Abbas, Iran.
2. Islamic Azad University, Bandar Abbas Branch, Iran
3 University of Applied Science and Technology, Bandar Abbas ACECR Center, Iran

Received 18 October 2013; accepted 10 March 2014

Abstract

The Tazerj travertine deposits are located 25 km northwest of Haji Abad and 5 km northeast of Tazerj Village in Hormozgan Province, southern Iran. This area is part of the Folded Zagros Zone. The studied travertine deposits are located on Eocene deposits and were most likely formed through the dissolution and re-deposition of groundwater and atmospheric waters onto the Asmari limestone. The petrographic evidence shows calcite to be the dominant mineral forming the microscopic sections of the Tazerj travertine deposits. The textural characteristics of the sediments confirm that microbial and biological activity was present at the time of deposition. XRD results confirm the existence of calcite-type calcium carbonate. In addition, XRF results confirm low levels of strontium and relatively high levels of magnesium. Finally, the geological evidence indicates that the rocks were created as a result of tectonic activity. The circulation of atmospheric deep water and its reappearance on the ground as hot springs through fractures and faults, formed meteogenic travertine deposits in Tazerj along large faults and fractures. The temperature of the hot springs responsible for creating the travertine deposits is estimated at approximately 30 °C.

Keywords: *travertine, calcite, tectonic, metogene, Tazerj*

1. Introduction

Travertine deposits are limestone rocks formed by the deposition of carbonate sediments from hot springs containing high levels of Ca^{2+} with a high partial pressure of carbon dioxide (pCO_2) [1]. Generally, during the formation of travertine deposits hot acidic water passes through carbonate rocks, particularly limestone, dissolving calcium carbonate and transferring it to the ground as a carbonate and bicarbonate solution. A carbonated travertine deposit forms on the ground due to the depressurization and degassing of CO_2, increasing pH, mineral saturation and volatilization [2, 3]. Stable conditions and the constant formation of carbonated layers creates uniform layers of porous carbonated sediment (travertine) with a thickness ranging from a few centimeters to several meters. In most cases, a gentle slope is present on the oldest rock layers [4]. Spring carbonates precipitate at various sedimentation sites. Based on field evidence, a pattern cannot be presented to categorize all spring carbonates (e.g. Tufa and travertine, [5, 6]). Generally, four chemical processes form travertine deposits [3]. 1- Deposition of acidic water containing calcium ions according to the reaction (1):

$$Ca^{2+} + 2\,(HCO_3^-) = CaCO_3 + CO_2 + H_2O \qquad (1)$$

2- A small number of travertine deposits are formed by the reaction of atmospheric carbon dioxide with hyper alkaline ground water according to the reaction (2):

$$Ca\,(OH)_2 + CO_2 = CaCO_3 + H_2O \qquad (2)$$

3- Some travertine deposits form by a combination of calcium-rich groundwater with alkaline surface water. Hydroxyl ions from lake waters react with bicarbonate ions (HCO^{3-}) to form $(CO_3)^{2-}$ ions eventually leading to a deposition of calcium carbonate according to the reaction (3):

$$Ca\,(HCO_3)_2 + OH^- = CaCO_3 + HCO_3^- + H_2O \qquad (3)$$

4- Calcium carbonate can form due to the escape or release of CO_2 along with increased concentrations of Ca in the fluid due to its reaction with hydroxyl ions.

Most travertine deposits consist of two types of calcium carbonate polymorphs including calcite and aragonite. Conditions under which these minerals form depend on factors such as the chemical composition of the source water, temperature, pressure and the rate of release of CO_2. Calcium carbonate constitutes more than 95% of travertine deposits. The polymorphs greatly assist in identifying the conditions under which the travertine deposits formed. The travertine type is dependent on the composition of the source water. Travertine deposits formed by a water source along with material transported from surface layers are known as meteogenic travertine. In contrast, travertine

---

*Corresponding author.

E-mail address (es): abedpour.z@gmail.com

deposits formed by a water source along with material transported from deep layers with thermal activity are called thermogenic travertine [3]. Iran is one of the main travertine producers in the world. Most of the extracted travertine is consumed domestically with less attention being paid to the world market. Travertine mines in Iran include: the Azarshahr Mine in eastern Azerbaijan, Sardarabad Mine in Ardestan and Natanz, Ananr and Sarcheshmeh Mines in Kerman and the Firoozkooh Mine in Tehran. The travertine deposits studied in this paper are located 5km from Tazerj Village near Madanouyeh Spring in northern Hormozgan [7] (Fig. 1).

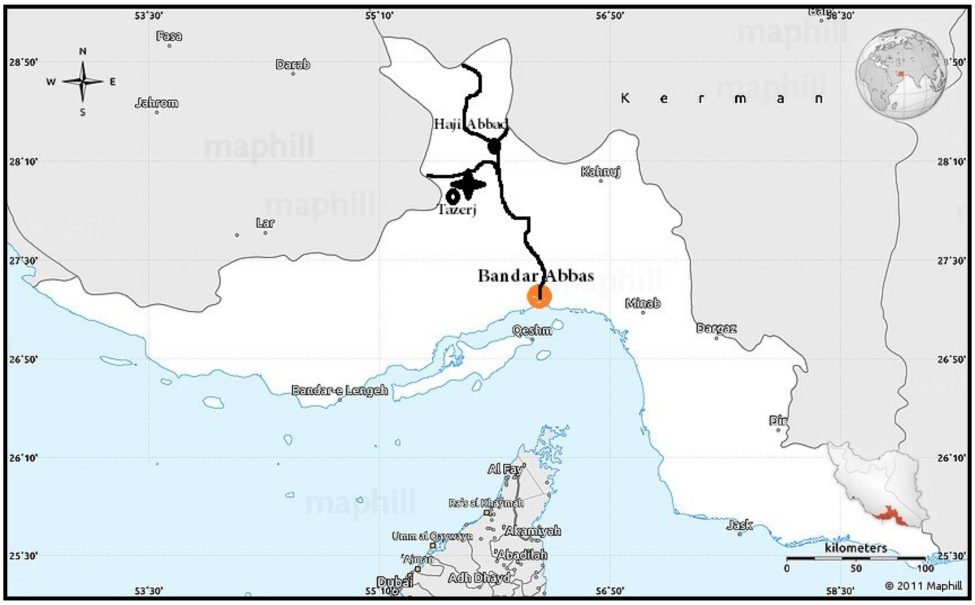

Fig. 1: Map showing the geographic location of the studied travertine in Hormozgan Province, Iran

2. Methods

Six fresh samples (1kg) collected from the travertine layers of the study area at a depth of 3-5m were sent to Kansaran Binalood Laboratory for mineralogical, petrographic and geochemical evaluation. The mineralogical composition of the samples was determined by X- ray powder diffraction (XRD) using a PHILIPS/ model: PW 1800 diffractometer running at 40Kv and 20Ma using CuKα radiation. Quantitative analysis of major and minor elements was determined by X- ray fluorescence (XRF) using a PHILIPS/ model: PW 1480 spectrometer with analytical uncertainties ranging from 1% to 3%. Trace element and REE concentrations were determined using inductively coupled plasma mass spectrometry (ICP-MS).

3. Regional Geological Setting

The Tazerj travertine deposit is located in the Folded Zagros (Fig 2a). The Zagros fold and thrust belt (Zagros FTB) is an approximately 1,800 kilometer (1,100 mi) long zone of deformed crustal rock, formed in the foreland of the collision between the Arabian Plate and the Eurasian Plate (Fig 2b). Host to one of the world's largest petroleum provinces, it contains approximately 49% of the established hydrocarbon reserves in fold and thrust belts and about 7% of all reserves globally [8]. The Zagros FTB is formed along a section of the plate boundary that is subject to oblique convergence with the Arabian Plate moving northwards with respect to the Eurasian Plate, at approximately 3 cm per year. The degree of obliqueness reduces southwards along the Zagros, with the collision becoming near orthogonal within the Fars domain [9].

Travertines located in Eocene and Oligo-Miocene units of the Asmari-Jahrom limestone are abundant in the studied area (Fig 2c). In the southeastern range near Gahkom Village, non-distinctive Asmari and Jahrom formations appear in the Siro Mountains and the eastern highlands. Jahrom formations do not appear on their own in the study area. The extended Asmari formation includes much of the Tazerj travertine deposit. Tectonically, the study area is active and influenced by Zagros thrust faults. There are many small faults in the range limited by the thrust sub-faults and Planzh Baraftab stalagmite from the south and humilities limestone of mixed color zone along with Orbitolina-bearing limestone of the Razdar Mountains from the north and northeast.

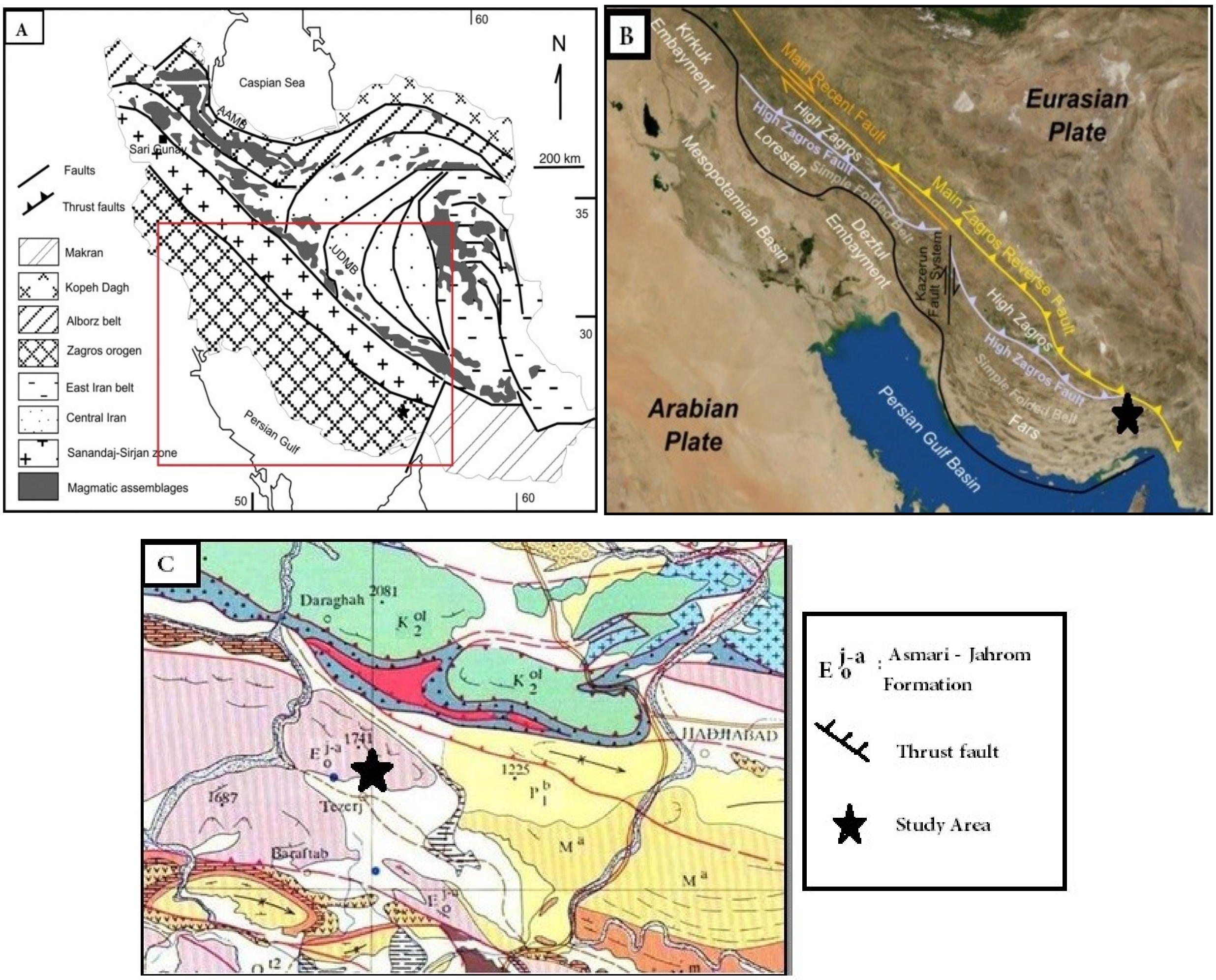

Fig. 2: (a) Structural map showing location of Tazerj travertine (b) Zagros Zone, collision between the Arabian Plate and the Eurasian Plate [8] (c) Haji Abbad geological map, 1:250,000 scale, showing location of study area

4. Lithology

Limestone units in the study area appear as horizontal layers with a slight slope toward the southwest. The surface sections are severely weathered and crushed, displaying holes in some portions. While the size of the holes in the travertine deposits varies greatly, the average diameter of most holes measures approximately 2 to 3 mm (Fig. 3). Also observed were holes with a diameter ranging from approximately 10 to 20 centimeters. These larger holes most likely formed due to the existence of impurities and barriers at the time of deposition of the main unit, but could also be cavities formed by groundwater during later periods. Because they create limitations for façade application, they are highly undesirable. Also in existence are horizontal limestone travertine deposits containing worm tubes and trace fossils of living organisms. Worms living near the hot springs created small tunnels. There have been similar findings in the Asmari formation in other regions of Iran (including Fars). Unfortunately, the presence of these worm tunnels has created relatively large voids, as shown in Figure 4, lowering the quality of the ore minerals for façade applications.

Among other features of the travertine rock units in the study area are small and large cracks on the surface. Due to the active tectonics of the zone and intense physical weathering, this was expected. However, excavations of the site showed a higher density of cracks at greater depths. Therefore, a large portion of the travertine outcrop in the study area is unusable as façade stone due to the numerous fractures, cracks, worm tubes and cavities. Figure 5 shows the density of the surface and deep wall cracks.

Fig. 3: *Travertine outcrops with various holes*

Fig. 4*: Small channels (worm tubes) and organic material in the travertines*

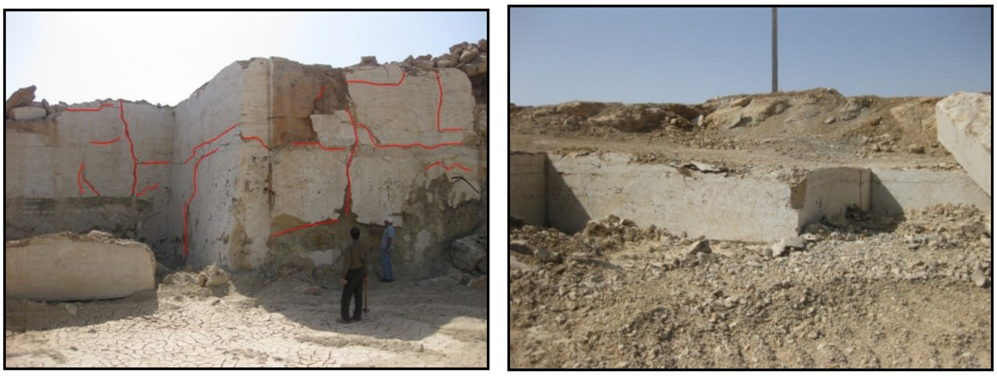

Fig. 5*: Numerous cracks in the surface travertines and cracks in deep walls*

5. Petrography

In order to specify the minerals and regional travertine fabric, six samples with different fabrics were taken and thin microscopic sections were prepared. Microscopic study of the travertine revealed that most of the calcium carbonate (calcite) crystals formed porous bands. The calcite crystals displayed different growth rates, sizes, and shapes (Fig. 6 a and b). The voids and porosities, formed mainly by the fermentation and decomposition of organic matter such as algae, filled with large secondary crystals of sparite carbonate (Fig. 6c). Some of the calcium carbonate samples contained laminated structures. Additionally, there was evidence of fertilization along some of the calcite bands and portions of the fabric (Fig. 6 d). According to the classification of carbonate rocks [10], these are classified as boundstone composed of calcite and algal organic laminates.

6. Geochemistry

Although aragonite is less stable than calcite at room temperature, it forms extensively in nature near hot springs. Numerous experiments have shown that aragonite preferably forms from water with a temperature of 30 to 60 °C. At lower temperatures, aragonite usually forms with a high concentration of magnesium [11, 12].

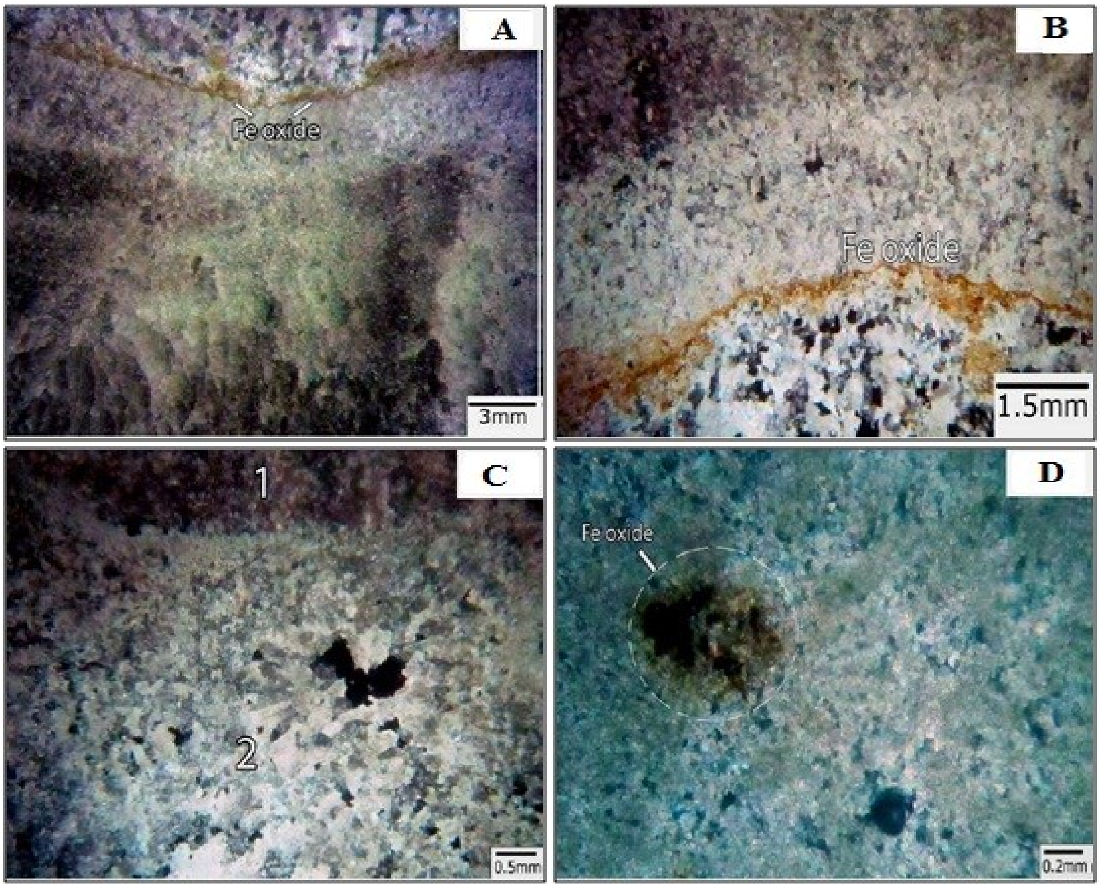

Fig. 6: Microscopic section T2 sample (XPL) : (A, B) growth rate, size, and different shapes of calcite crystals (C) 1:calite fine grain matrix 2: filled voids and porosities with secondary large crystals of sparite carbonate (D) fertilization parts along some calcite matrix

Recent studies [13] indicate that aragonite forms in waters with a temperature higher than 44 °C. Calcite and aragonite form at temperatures between 30 and 43 °C and calcite forms at temperatures less than 30 °C. The formation of aragonite at temperatures less than 30 °C is dependent on other factors such as the concentration of magnesium, strontium, and organic materials.

According to the results of phase analysis listed in Table 1 and Figures 7 and 8, the carbonate calcium in the Tazerj travertine deposits is of calcite-type. This indicates that the temperature of the hot springs responsible for forming the travertine was probably less than 30 °C. The specific calcium carbonate type is identifiable using X-ray fluorescence (XRF) and inductively coupled plasma (ICP) analysis. Aragonite-type travertine can contain high levels of strontium and lead while calcite-type travertine usually contains lower concentrations of these. In addition, calcite-type travertine deposits contain higher magnesium levels than aragonite-type travertine [4].

In this study, a list of major and trace elements contained in the Tazerj travertine deposits was compared to the elements contained in calcite and aragonite-type travertine deposits. Dickson (1990) proposed a model based on the Sr/Ca ratio. According to Dickson's model, calcite forms at Sr/Ca ratios less than 0.001. Phase analysis along with strontium levels obtained from chemical analysis (Table 2), show that the travertine samples are of calcite type. Low levels of strontium (486- 2180 ppm) in the samples, compared to the Sr content in the aragonite-type travertines (9500 ppm), show that the Tazerj travertine deposits are of calcite type (Fig. 9).

Table 1*: XRD results of Tazerj travertine*

sample	Major phase	Minor phase
T1	calcite	quartz
T2	calcite	________
T5	calcite	Quartz , anorthite
T3a	calcite	quartz
T4a	calcite	Quartz, anorthite
T4b	calcite	Quartz, chlorite

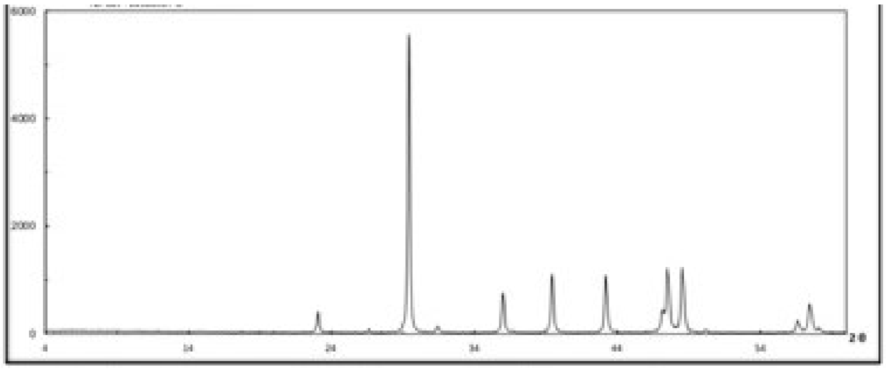

Fig. 7*: XRD diagram of T1 sample*

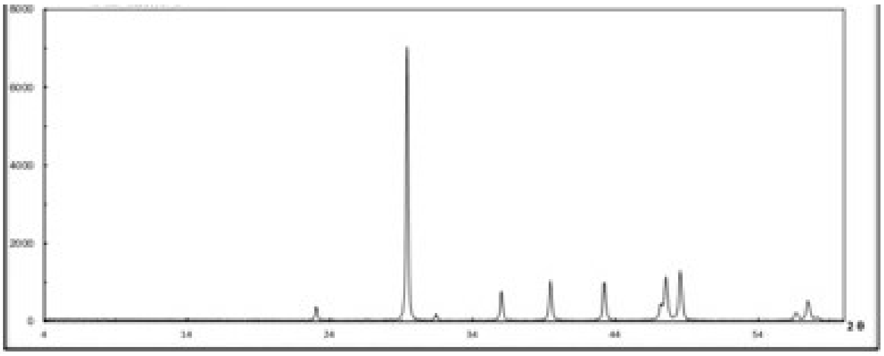

Fig. 8*: XRD diagram of T2 sample*

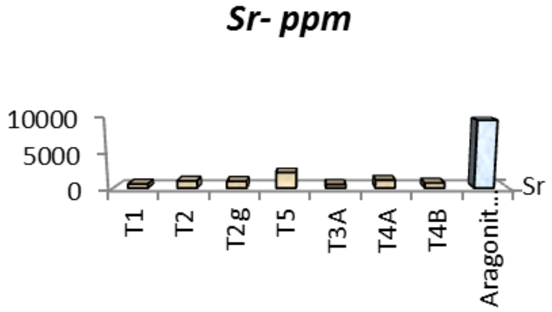

Fig. 9*: Comparison of Sr content in study samples with aragonite-type travertines*

Magnesium forms a solid solution series with calcium in calcite and makes a wide variety of changes possible. In most travertine deposits, magnesium does not replace calcium. As a result, calcite containing high magnesium levels is rare. Figure 10 shows the concentration of magnesium in the travertine deposits. This data suggests that a small number of meteogenic travertine deposits formed from calcites with a maximum Mg level of 1 wt. % (Fig. 10a). The thermogenic travertine deposits formed with a magnesium content similar to that found in the meteogenic travertine deposits (Fig. 10b). However, a small number of samples were found with a magnesium concentration of 1.0 wt. %, common in meteogenic travertine deposits. Aragonite-type travertine contains lower magnesium levels than calcite-type travertine (Fig 10c). Tazerj travertine contains 0.15 to 0.31 weight % Mg (Table 2) compared to higher levels of magnesium found in aragonite travertine. This confirms that the travertine deposits in Tazerj are of calcite-type.

According to Kitano (1963), manganese tends to co-precipitate with iron when the iron content in water is high. In contrast, when iron levels are low, manganese tends to enter into the crystal lattice of calcium carbonate. Iron and divalent manganese also exists in the precipitating calcites. Although travertine deposits form through oxidation, when divalent iron is scarce, less substitution occurs. The water-saturated travertine deposits are identified by the associated organic matter. Iron oxide can reduce substantially in these travertine deposits and change to calcite during the digenesis process. Divalent manganese may remain in the solution longer, entering the calcite crystal lattice under oxidation conditions.

Some travertine samples, almost white in color, contain only a trace amount of iron oxide. Travertine deposits with low iron content (1000- 4000 ppm) are brown due to the presence of organic matter. Based on analysis, most travertine deposits are yellow and brown because of organic matter concentrations [14]. The average iron content in meteogenic and thermogenic travertine deposits is 0.16 and 0.26 wt. %, respectively.

Manganese forming a solid solution series with calcite is rarely seen in large quanties. The average manganese content in meteogenic and thermogenic travertine deposits is 0.012 and 0.091 wt. %, respectively [2]. The iron and manganese content in the samples studied was 0.14 to 0.38 and 0.15 to 0.37 wt. %, respectively.

Table 2: Strontium and Magnesium content of the studied samples and Aragonite type travertines

Element (ppm)	**T1**	**T2**	**T5**	**T3A**	**T4A**	**T4B**	**T2G**	**Aragonitre Type**
Sr	540	990	2180	486	1109	689	940	9500
Mg	0.21	0.22	0.31	0.25	0.27	0.15	0.22	____

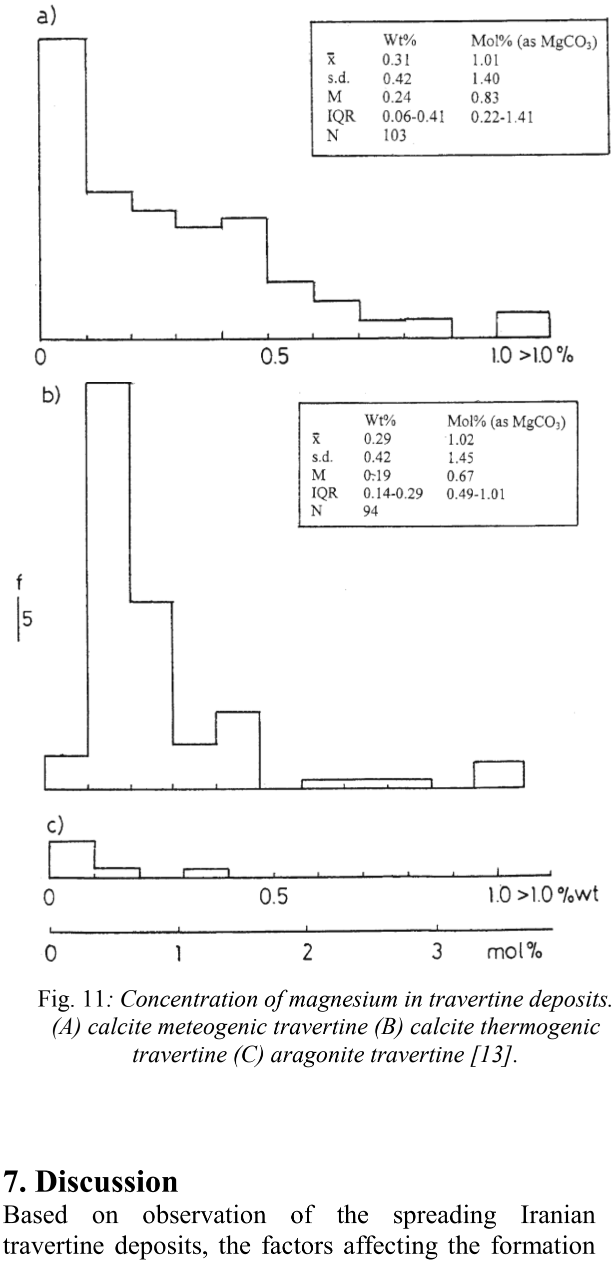

Fig. 11*: Concentration of magnesium in travertine deposits. (A) calcite meteogenic travertine (B) calcite thermogenic travertine (C) aragonite travertine [13].*

7. Discussion

Based on observation of the spreading Iranian travertine deposits, the factors affecting the formation of travertine rocks was examined. Volcanic activity is probably the main factor in the formation of travertine deposits on the hot marble strip in Iran [15]. The periodic fluctuation of thermal geological activity, volcanic ascending and descending, annual changes and the varied physicochemical composition of thermal waters can all effect and cause color changes in travertine deposits (Fig. 11) [15].

The calcium carbonate polymorph type greatly helps to define the conditions under which the travertine deposits formed. Microscopic pictures show that a type of calcium carbonate is the main mineral. According to the XRD analysis results listed in Table 1 and Figures 8 and 9, the calcium carbonate in the Tazerj travertine deposits is of calcite-type. This indicates that the temperature of the thermal springs forming the travertine was probably less than 30 °C. Table 3 shows the major elemental composition of the Tazerj travertine deposits compared to standard limestone, meteogenic and thermogenic travertines. According to the results, the Tazerj travertine deposits resemble meteogenic travertines and therefore, are considered to be of meteogenic type. The study area is part of the Zagros Zone and does not experience volcanic or plutonic activity. Therefore, the travertine deposits in Tazerj are not of thermogenic type. Geochemical test results further confirm this.

The limestone deposits in Tazerj left by springs are mainly marble-free travertine (calcite). Micro-thin aragonite layers composed of thin, needlelike crystals of aragonite exist in the travertine deposits. In general, the deposits left by the springs in Tazerj are mainly composed of travertine. It is not clear why the deposits in the Tazerj region are marble-free. It is possible that weather conditions, a shortage of CO_2, an alkaline environment, low water temperatures and high levels of bicarbonate solution led to the formation of travertine in the area. The travertine layer forms a semi-lens (a lens with a flat surface) on the Asmari limestone where the spring forming the travertine most likely flowed. The textural characteristics of the sediments confirm the presence of microbial and biological activity at the time of deposition. Geological evidence indicates that the rocks are the result of tectonic activity. Faults and fractures play a major role in the circulation and rise of thermal fluids in the geothermal areas [16, 17]. The circulation of deep atmospheric water and its reappearance on the surface through fractures and faults formed meteogenic travertine deposits.

Table 3*: Comparison of elemental content of Standard Limestone, Metogene Travertine, Thermogene Travertine and Mean of Tazerj Travertine [18]*

Elements	Mean of Standard Limestone	Metogene Travertine	Thermogene Travertine	Mean of Tazerj Travertine
Si	24000	< 140 > 22000	100 -0> 32000	12133
Al	4200	100 - 15000	410 - 8200	4150
Fe	3800	46 - > 4000	< 50 -0> 37000	2167
Na	400	200 - 1300	7 - 2940	562
K	2700	147 - 5500	8 - 5500	608
Mg	47000	180 - > 8000	60 - > 35000	2225
Ti	400	< 30- 2370	0 -3000	144
Mn	1100	5 -01600	8 - > 3400	99
P	400	8 - 950	9 - 220	299
S	1200	240- 14000	14 - 7400	2900
Cl	150	< 80 - 850	< 20 - 9000	96.3
Ba	10	2 - 10000	2 - > 32000	31.6
Sr	610	9 - >2930	20 -14000	999
Cu	4	< 0.5 - 96	4 - 188	3.33
Zn	15 - 38	4 - 680	5 - 98	9.16
Pb	1.5 - 9	< 2 - 31	2 - 228	10.3
Ni	20	4 - 116	< 1 - 15	35.8
Cr	11	< 1 -117	<1 - 146	4.5
Ag	__	< 23	< 2.8	0.49
As	1	<3 - 363	150 - > 1600	2.5
Be	__	0.05 – 1.2	1.4 - 15	< 0.2
Cd	0.04	__	__	0.23
Ce	11.5	__	1 - 126	8
Co	0.1	< 1 - 428	< 1 - 140	2
La	__	__	< 1 - 145	3
Li	5	<0.05 – 1.7	< 1 -10	2
Mo	0.4	1 - 63	< 100	1.03
Sb	0.2	< 5 -11	__	1.05
Sc	1	< 0.5 – 0.7	< 100	0.8
Sn	___	<30	< 100	3.1
Th	1.7	0.1 – 0.4	__	6.7
U	2.2	0.4 – 0.7	< 1 - > 500	< 0.2
V	20	< 2 - 413	1 - 100	7
Zr	19	< 0.5 - 192	12 - 132	6

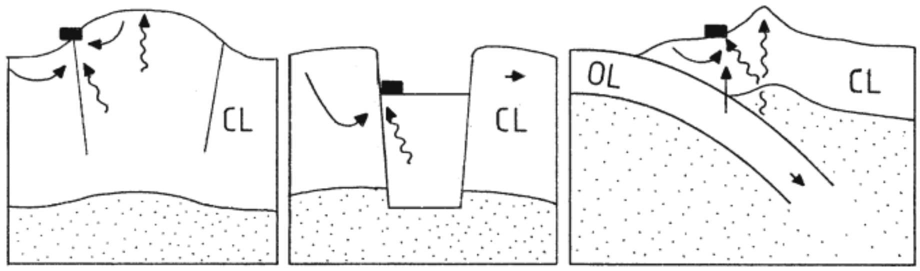

Fig. 11*: Travertine, volcanism and plate tectonics. (a) hot spot volcanic and associated hydrothermal activity (b)rift (c) continental margin volcano. Short arrow shows plate movements; curly arrow, CO2 flux; long arrow, water flow. Stippled area -Asthenosphere, CL -continental lithosphere, OL -oceanic lithosphere. Black boxes show position of thermogene travertine formation.*

8. Conclusion

The Tazerj travertine deposits are located in the Folded Zagros Zone and limestone units of the Asmari-Jahrom Formation of Eocene/Oligo-Miocene age. Based on petrographic studies, the Tazerj travertine deposits are mainly composed of calcium carbonate (calcite) crystals as porous bands. Secondary sparite carbonates fill the voids and porosities. According to XRD results, the calcium carbonate in this travertine deposit is of calcite type. Results show that the temperature of the springs that formed the travertine deposit was probably less than 30 °C. A comparison of the average elemental content (XRF) of meteogenic and thermogenic travertines to the Tazerj travertine deposits shows it to be of meteogenice-type. The study area is a part of the Zagros Zone and does not experience volcanic or plutonic activity. Therefore, the Tazerj travertine deposit is not of thermogenic type.

Acknowledgements

The authors would like to express their gratitude to Islamic Azad University of Bandar Abbas for their sponsorship.

References

[1] Ford, T.D., and Pedley, H.M., 1992, Tufa deposits of the world', J. Speleol. Soc. Japan, v.17, p. 46–63.

[2] Kitano, Y., 1963, Geochemistry of calcareous deposits found in hot springs.' J. Earth Sci. Nagoya Univ., v.11, p. 68–100.

[3] Pentecost, A., 2005, Travertine. Springer – verlag Berlin Heidelberg, printed in the Netherlands, 445 p.

[4] Takashima, C., Okumura, T., Nishida, S., Koike, H., and Kano, A., 2011, Bacterial symbiosis forming laminated iron-rich deposits in Okuoku-hachikurou hot spring, Akita Prefecture, Japan. Island Arc, v. 20, p. 294– 304.

[5] Capezzuoli, E., Gandin, A., and Pedley, H.M., 2013, Decoding tufa and travertine (fresh water carbonates) in the sedimentary record: The state of the art Sedimentology. doi:10.1111/sed.12075.

[6] Jones, B., and Renaut, R. W., 2010, Calcareous spring deposits in continental settings, Developments in Sedimentology, v. 61, p. 177–224.

[7] Talebian, M.; Jackson J., 2004, A reappraisal of earthquake focal mechanisms and active shortening in the Zagros mountains of Iran, Geophysics Journal International, v. 156 (3), p. 506 – 526.

[8] Cooper, M., 2007, Structural style and hydrocarbon prospectively in fold and thrust belts: a global review. In Ries A.C., Butler R.W. & Graham R.H. Deformation of the Continental Crust: The Legacy of Mike Coward, Special Publications, v. 272. London: Geological Society, p. 447–472.

[9] Tarrah, S.J. and Khorshidi, E., 2013, Petrography and phisico – chemical Tazerj travertine in the Haji Abbad. Research project, Islamic Azad University, Bandar Abbas branch, 109p.

[10] Dunham, R.J., 1962, Classification of Carbonate Rocks According to Depositional Texture. In, W.E. Hamm (Ed.), Classification of Carbonate Rocks, A Symposium. American Association of Petroleum Geologists, p. 108-121.

[11] Folk, R.L., (1994), Interaction between bacteria, Nano bacteria, and mineral precipitation in hot springs of central Italy', Géogr. Phys. Quat., v.48, p. 233–246.

[12] Lippmann, F., 1973, Sedimentary Carbonate Minerals, 228 p, Heidelberg (Springer-Verlag).

[13] Fouke, B.W., Farmer, J.D., Des Marais, D.J., Pratt, L., Sturchio, N.C., Burns, P.C., and 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.)', J. Sed. Res., 70, 565–585 with calcium carbonate deposition', Cave Karst Sci., v. 27, p. 71–78.

[14] White, W.B., 1981, Reflectance spectra and color in speleothems, Nat. Spel. Soc. Bull., v. 43, p. 20–26..

[15] Momenzadeh. M., and Haidari, A., 1988, Geographical spread of biostratigraphy and decorative stones. The first symposium of Iran decorative stones.

[16] De Filippis, L., Faccenna, C., Billi, A., Anzalone, E., Brilli, M., Ozkul, M., Soligo, M., Tuccimei, P., and Villa, M., 2012, Growth of fissure ridge travertine from geothermal springs of Denizli Basin, western Turkey, Geol. Soc. Am. Bull., v. 124, p. 1629–1645.

[17] Von Wintzingerode, F., Gobel, U. B., and Stackebrandt, E., 1997, Determination of microbial diversity in environmental samples: Pitfalls of PCR-based rRNA analysis. FEMS Microbiology Reviews, v. 21, p. 213–29

[18] Turekian, K.K. and Wedepohl, K.H., 1961, Distribution of elements in some major units of the earth's crust', Bull. Geol. Soc. Am., v. 72, p. 175–182.