

Geochemistry of Carbon, Oxygen and Sulfur Isotopes in Soils along a Climotoposequence in Kerman Province, Central Iran

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ABSTRACT

Carbon and sulfur isotopic data are helpful in understanding environmental conditions under which soils are formed. Soils from 18 sampling sites along a climotoposequence from higher Laleh Zar Mountains (4,351 m above sea level with xeric-mesic soil moisture-temperature regimes) to Shahdad depression (250 m above sea level with arid-hyperthermic soil moisture-temperature regimes) in Kerman Province, central Iran, were studied. $\delta^{13}\text{C}$ values of the soil organic carbon varied between -20.6‰ and -26.9‰ PDB. $\delta^{13}\text{C}$ values of pedogenic carbonates varied between -2.2‰ and $+2.2\text{‰}$ PDB and a decreasing trend was observed downward in the climotoposequence. A positive correlation ($r=0.6$) was found between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in the lower arid landscape, but a different relationship ($r=0.37$) in the upper Mediterranean climatic positions was observed. It seems that the presence of more C3 plants under stress and more decomposition of organic matter in lower positions of the landscape has taken place. $\delta^{13}\text{C}$ values of soil organic carbon and pedogenic carbonates and their trend along the gradient showed that higher proportion of C3 plants at lower elevations and presence of more C4 plants in the past history of upper landscape positions may have been experienced. Mean $\delta^{34}\text{S}$ value of 11.3‰ showed that lower Cretaceous sea sulfate may have been the source of sulfur in the area. Mean δD and $\delta^{18}\text{O}$ values of -51.2‰ and $+6.0\text{‰}$ in gypsum crystallization water showed that direct deposition from a solution saturated with gypsum is the only probable mechanism of gypsum formation in the area.

Keywords: Gypsum crystallization water, Pedogenic carbonate, Soil organic carbon, Stable isotope geochemistry.

INTRODUCTION

Information on the amount and accumulation rate of pedogenic carbonate in soils helps estimation of carbon pools and fluxes and past climatic conditions in terrestrial environments, which also reflects the influence of paleoclimate in a given area (Landi *et al.*, 2003). Carbon isotope ratios in both organic and inorganic soil materials

could help to establish the kind of processes and the environmental conditions involved in soil formation (Boutton, 1996; Cerling and Hay, 1986). Carbon isotopic data were also used to study the mechanisms of carbon dissolution and precipitation (Mermut *et al.*, 2000; Nordt *et al.*, 1996) and to understand the carbon cycle (Salehi *et al.*, 2004).

There is a substantial difference in ^{13}C discrimination in the photosynthetic pathways of C3 vs. C4 plants with mean δ

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^{13}C values of -27 and -12 ‰, respectively (Cerling and Quade, 1993; O'Leary, 1988). In the absence of C3-C4 vegetation shifts, other ecological factors affect carbon isotope values in the soil (Stevenson *et al.*, 2005).

Mode of pedogenic carbonate formation studied by Khademi and Mermut (1999) in Isfahan area of central Iran, with an arid soil moisture regime, showed that carbonates were formed in an environment with more available moisture and higher proportion of C4 plants than observed today. In a similar study in the west central Iran, with a xeric soil moisture regime, Salehi *et al.* (2004) found that current vegetation consists of C3 plants, but soil pedogenic carbonate was formed in conditions with a lower proportion of C3 plant species and the shift of C3-C4 vegetation was attributed to human induced land degradation. The stable carbon isotope geochemistry of organic carbon and pedogenic carbonate in soils along a climosequence in Saskatchewan soils of Canada (Landi *et al.*, 2003) and soils of Washington state, USA (Stevenson *et al.*, 2005) showed a good relation between $\delta^{13}\text{C}$ values and mean annual precipitation.

Gypsiferous soils cover about two hundred million hectares in the world (Nettelton, 1991). Origin of gypsum and more soluble salts in these types of soils has been studied by several researchers. Sofer (1978) described three important geochemical processes of gypsum formation including oxidation of sulfide minerals, hydration of anhydrite, and direct deposition from an evaporating solution saturated with gypsum. Pyrite oxidation has been reported as the major source of gypsum by Mermut and Arshad (1987) and Dowuona *et al.* (1992a, b). Khademi *et al.* (1997a) found that lower Cretaceous sea sediment is the source of sulfate in Isfahan region, central Iran. Farpoor *et al.* (2004) suggested that in southeastern Iranian soils, gypsum was formed through direct deposition of the Thetian sea lagoons, similar to gypsum formation in central Iran. Using the stable isotope geochemistry of sulfur bearing minerals in soils and sediments from

different geomorphic surfaces in Loot Desert of central Iran, Farpoor and Krouse (2008) attempted to explain the evolution of the geomorphic surfaces in that area. Genesis of gypsum enriched soils in north-west Isfahan, central Iran was also studied by Toomanian *et al.* (2001).

The objectives of the present research were to: (1) determine the carbon isotope geochemistry of pedogenic carbonates and soil organic matter along a climotoposequence from Laleh Zar elevations to Shahdad depression, (2) study the S and O isotope geochemistry in the area, (3) investigate the $\delta^{18}\text{O}$ and δD values of gypsum crystallization water, and (4) establish the mode of gypsum and carbonate formation in the area.

MATERIALS AND METHODS

Study Area and Sampling

The study site is located in the Kerman Province, southeastern part of central Iran (Figure 1). The climotoposequence under study extends from Laleh Zar with an elevation of 4351 m asl (above sea level) in the south west to the Shahdad depression, 250 m asl in the north-east (Figure 2).

Mean annual precipitation in the area ranges between 250 mm (in the south-west) and 50 mm (in the north-east). Soil moisture and temperature regimes change from xeric and mesic in the Laleh Zar Mountain to aridic and hyperthermic in the Shahdad area near the Loot playa.

Geological formations are dominated by igneous formations and volcanic tuffs in the south-west to limestone and Neogene Formations in the north-east of the transect. Soil samples, secondary carbonates, and gypsum crystals were collected from 18 sites along the transect (Figure 2).

Due to the extent of the area and soil variations along the studied transect, sampling for organic carbon, pedogenic carbonates, soluble sulfates, and crystallization water of gypsum analyses

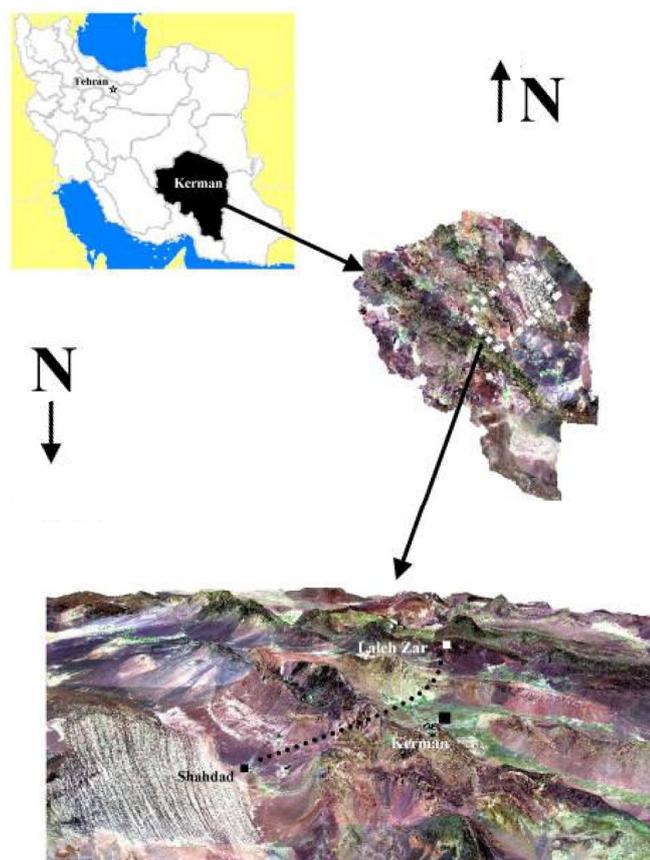


Figure 1. Location of the study area.

was performed in appropriate sites. Site 1 was located at higher elevations of the transect. Histosols were dominant soils in this site (Table 1). Moving down the slope, soil moisture decreased, so that in site 6, xeric moisture regime shifted to aridic. Organic matter content showed also a decreasing trend toward downslope positions (about 0 %). That is why organic carbon samples were only collected from sites 1-9 on the transect.

On the other hand, C and O isotopes of pedogenic carbonates were measured in the soft mass and carbonate nodules were sampled only from sites containing Bk horizons. Moving down the slope toward site 18 (near Loot Desert), the amount of soluble sulfates increased, but S and O isotopes determination were performed on soils of all 18 sites studied. Besides, four pure gypsum samples from sites 8, 11, and

12 were also collected for gypsum crystallization water analyses and no pure gypsum crystals were found in other sites studied.

Laboratory Studies

For inorganic carbon isotopic composition analysis, a sample containing approximately 10 mg of pedogenic carbonate was placed in the main portion of the Y-shaped reaction vessel, keeping the sample off the side walls and out of the side arm. An extra amount of 100% phosphoric acid (about 4 mL) was placed in the side arm. The vacuum system was used to evacuate the reaction vessel. The phosphoric acid was tipped into the sample chamber after evacuation and left overnight for the reaction with soil carbonates (Boutton, 1991; Khademi and

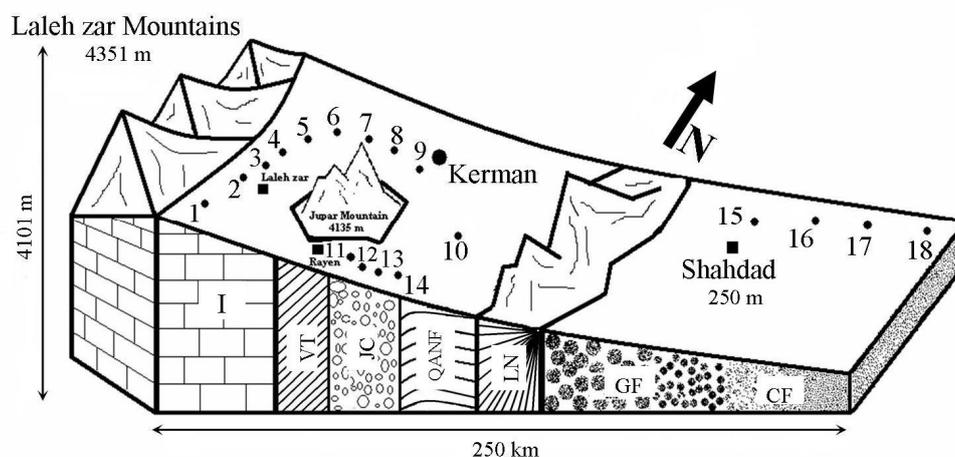


Figure 2. The studied transect showing sampling sites. I: Igneous; VT: Volcanic Tuffs; JC: Jupar Conglomerate; QANF: Quaternary Alluvium, Neogene Formation; LN: Limestone, Neogene; GF: Gravel Fan; CF: Clay Flat.

Mermut, 1999). Using the vacuum system on the next day, the liberated CO₂ gas was purified and utilized for analysis. The CO₂ gas derived from the above mentioned procedure can be used for both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ measurements of the samples, because the oxygen in the CO₂ generated from

carbonate acidification is derived from carbonates.

Soil organic carbon samples were also analyzed for carbon isotopic composition. Samples were soaked in an excess amount of 3M HCl at room temperature overnight to remove the carbonates (conversion of

Table 1. Selected environmental characteristics and soil classification of studied sites.

Site	Elevation(m)	Geomorphic Position	Soil classification ^a	Rainfall(mm)	Temperature (°C)
1	3072	Lowland	Haplohemists	227	9.7
2	3451	Lowland	Epiaquolls	227	9.7
3	3000	Piedmont Plain	Calcixerepts	NA ^b	NA
4	2800	Piedmont Plain	Natrixeralfs	NA	NA
5	2300	Piedmont Plain	Calcixerepts	NA	NA
6	2200	Piedmont Plain	Natrigypsids	NA	NA
7	2200	Piedmont Plain	Natrigypsids	NA	NA
8	2000	Rock Pediment	Haplosalids	151	15.7
9	1840	Alluvial Plain	Haplocalcids	151	15.7
10	1814	Alluvial Plain	Calcigypsids	140	16.5
11	2433	Rock Pediment	Haplogypsids	NA	NA
12	2127	Rock Pediment	Haplogypsids	NA	NA
13	2089	Rock Pediment	Haplogypsids	NA	NA
14	1788	Rock Pediment	Haplogypsids	NA	NA
15	278	Playa	Haplosalids	50	26
16	263	Playa	Aquisalids	50	26
17	261	Playa	Aquisalids	50	26
18	257	Playa	Aquisalids	50	26

^a Soil Survey Staff (2010).

^b Not available.

carbonate carbon to CO₂). Using a millipore filter and deionized water, the excess acid was then removed from the soil sample. The carbonate-free soil samples were dried at 110°C after leaching and used for stable isotope analysis of organic carbon (Khademi and Mermut, 1999).

Dry combustion procedure described by Boutton (1991) in an excess of oxygen was used to convert organic carbon of the samples to CO₂ for isotopic analysis. This procedure involved the combustion of samples in sealed, evacuated vycor tubes containing CuO as the source of oxygen at 850°C for 3 hours. Cryogenic distillation was used to separate the CO₂ from other combustion products. The separated CO₂ was collected for δ¹³C analysis.

All forms of sulfates (soluble and mineral forms) were converted to pure BaSO₄ for δ³⁴S and δ¹⁸O analysis according to the method described by Dowuouna *et al.* (1992a).

Gypsum crystallization water was extracted using the method described by Halas and Krouse (1982) and Gonfiantini and Fontes (1963). The CO₂-H₂O isotopic equilibration method of Epstein and Mayeda (1953) with the modification of Roether (1970) was used for O isotopic analysis. For H/D analyses, H₂ was prepared by reduction of H₂O with Zn as described by Coleman *et al.* (1982).

The isotopic composition of gypsum mother water was calculated using the following equation:

$$\alpha = (\delta_{wc} + 1000) / (\delta_{mw} + 1000)$$

Where δ_{wc} is the isotopic composition (δ¹⁸O or δD) of crystallization water and δ_{mw} is the isotopic composition for gypsum mother water. According to Gonfiantini and Fontes (1963), the α¹⁸O is 1.004 and according to Pradhananga and Matsuo (1985), the αD is 0.98.

RESULTS AND DISCUSSION

Stable Isotope Composition of Organic and Inorganic Carbon

Organic Carbon

δ¹³C values of the soil organic carbon varied between -20.6‰ (site 7) and -26.9‰ (site 1) PDB (Table 2). In the climotoposequence studied, the δ¹³C values showed an increase with decreasing elevation and precipitation (Figures 1 and 2). The δ¹³C values of C3 and C4 plants are reported to be between -25‰ and -32‰ and -10‰ and -14‰, respectively (Cerling and Quade, 1993). Under soil moisture stress conditions, the isotopic composition of C3 plants are several per mil enriched in ¹³C (Stevenson *et al.*, 2005; Salehi *et al.*, 2004; Delucia *et al.*, 1988; Ehleringer *et al.*, 1986). The δ¹³C values of -20‰ have been reported for C3 plants growing in arid environments where stomatal conductance is limited (Ehleringer *et al.*, 1991). This could be one plausible reason for increasing δ¹³C values toward arid parts of the transect studied. Thus, the carbon isotopic

Table 2. Isotopic composition of soil organic matter in selected soils from area studied.

Site	Horizon/layer	Depth (cm)	Organic carbon δ ¹³ C (‰), PDB
1	Oe1	0-60	-25.9
1	Oe2	60-90	-26.3
1	Bwg1	90-120	-26.9
1	Bwg2	120-150	-26.9
2	A	0-60	-26.7
3	Bkz	40-70	-24.0
4	Bkz	5-30	-22.0
5	Bkz	70-100	-21.1
7	Bktn	50-90	-20.6
9	Bk1	30-50	-23.9



composition of soil organic carbon in the area studied seems to be predominantly derived from C3 plants. Stevenson *et al.* (2005) have also found a similar trend in $\delta^{13}\text{C}$ values of soil organic carbon in a gradient from 200 to 500 mm precipitation.

Decomposition processes and discrimination against ^{13}C and preferential preservation of organic matter rich in ^{13}C would also result in a slight fractionation process (Monger *et al.*, 1998; Stevenson *et al.*, 2005). This could be a second possible reason for increased trend of $\delta^{13}\text{C}$ in soil organic carbon and could be attributed to the above mentioned fractionation process. Higher temperature and lower precipitation in the arid parts of the transect can cause a faster organic matter decomposition and hence enrichment in $\delta^{13}\text{C}$.

Inorganic Carbon

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of pedogenic carbonates formed as soft masses and nodules (Table 3) showed a correlation with an *r* value of 0.40 which was insignificant, but the *r* value changed from 0.37 in the elevated and humid-arid parts of the transect (sites 3-7) to 0.6 in the really arid positions (sites 9-14). The positive correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in pedogenic carbonates is already well established (Salomons and Mook, 1976). Because both isotopes are enriched in the remaining

HCO_3^- , during precipitation in such a system, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are, therefore, correlated. Schlesinger *et al.* (1989) found that the positive correlation of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ could also be related to seasonal variations in biotic processes that affect the carbonate deposition. Khademi and Mermut (1999) also found a positive correlation with an *r* value of 0.7 between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in pedogenic carbonates in Isfahan region of Iran, which is almost similar to the area under study. However, the *r* value in the more humid parts of the transect with a Mediterranean climate is as low as 0.4. Similarly, the soil pedogenic carbonates in Mediterranean climate of Australia, Greece and Turkey, did not show a correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in pedogenic carbonates (Cerling and Quade, 1993).

The $\delta^{13}\text{C}$ values of pedogenic carbonates decreased downward on the transect (Table 3). One reason could be the higher proportion of C3 plants at lower altitudes, due to a change from mesic to aridic conditions. Most desert scrub species are among C3 plants (Volkoff and Cerri, 1987). It is also possible that the pedogenic carbonates at higher elevations may have formed under a different paleoenvironment. Mean $\delta^{13}\text{C}$ values of pedogenic carbonates in the upslope positions (sites 1-7) of the area is much higher (+0.45‰), than the mean value reported by Salehi *et al.* (2004) in Chaharmahal Bakhtiari Province of Iran, with a Mediterranean climate (-5.02‰). In

Table 3. Carbon and oxygen isotopic composition of pedogenic carbonates of some selected soils.

Site	Horizon	Depth(cm)	Pedogenic (‰)	
			$\delta^{13}\text{C}$ (PDB)	$\delta^{18}\text{O}$ (SMOW)
3	Bkz	40-70	-2.2	+28.36
4	Bkz	5-30	+1.5	+32.56
4	Bktn	65-100	-	-
5	Bkz	70-100	+2.2	+28.96
7	Bktn	50-90	+0.3	+32.56
7	C	140-160	-	-
9	Bk1	30-50	+1.3	+36.86
9	C	85-110	-	-
10	Bk1	30-70	-1.4	+32.76
10	Bk2	70-90	-1.7	+32.56
13	Bk	40-80	-1.6	+26.86
14	Bk	30-70	-1.1	+25.96

the Isfahan region of Iran, with an arid climate, Khademi and Mermut (1999) reported a mean $\delta^{13}\text{C}$ value of -0.25‰ . It seems, therefore, that higher $\delta^{13}\text{C}$ value of pedogenic carbonates in the study area is due to higher proportion of C4 plants in the past.

As reported by Romanek *et al.* (1992), the $\delta^{13}\text{C}$ value of CaCO_3 is about 10% greater than that of the CO_2 in the soil atmosphere at 20°C . Adding the least amount of 4.4 ‰ diffusional enrichment to the above mentioned value, Cerling and Quade (1993) concluded that the total enrichment between the soil respired CO_2 and pedogenic carbonate is about 14.4‰ at 20°C . Khademi and Mermut (1999) showed that the $\delta^{13}\text{C}$ values of pedogenic carbonates in Isfahan region, central Iran, ranged between -2.1‰ and $+0.9\text{‰}$. With the 14.4‰ enrichment discussed above, they concluded that the respired CO_2 from which the pedogenic carbonate formed, had $\delta^{13}\text{C}$ values ranging between -16.5‰ and -13.5‰ , which is much higher than the $\delta^{13}\text{C}$ values of soil organic carbon in that studied area. A great proportion of more C4 plants in the history of the area, and a great contribution of a parent material with an isotopically heavier carbon are two possible reasons mentioned by Khademi and Mermut (1999) for the higher $\delta^{13}\text{C}$ values of pedogenic carbonates in the Isfahan region, although the former reason is much more emphasized.

Considering the range of $\delta^{13}\text{C}$ values of -2.2‰ to $+2.2\text{‰}$ for the pedogenic carbonate of this research area (Table 3), it is calculated that the respired CO_2 has had the $\delta^{13}\text{C}$ values ranging between -16.6‰ and -12.2‰ , which are much higher than the $\delta^{13}\text{C}$ values of soil organic carbon (Table 2). This is even higher than the value reported in the Isfahan region. It is concluded that much of the pedogenic carbonates in this study area were precipitated in a much drier period. The $\delta^{13}\text{C}$ values of pedogenic carbonates are 21.9‰ , heavier than the mean $\delta^{13}\text{C}$ value

(-24.1‰) of soil organic carbon in the area.

Sulfur Isotope Geochemistry

Figure 2 shows the sampling sites for sulfur geochemistry studies. The summary of isotopic composition of sulfur and oxygen is given in Table 4. Although soil samples from all sites were used for sulfur isotope investigations, no gypsum or other soluble sulfates was found at the higher elevations of the transect (sites 1-5). Samples with gypsum taken from the lower slope position and depression (sites 6-18) had $\delta^{34}\text{S}$ values ranging between 7.7‰ and 12.6‰ (with a mean value of 11.3‰) and $\delta^{18}\text{O}$ values ranging between 7.2‰ and 17.8‰ (with a mean value of 11.3‰).

No trend in sulfur and oxygen isotope data regarding the change in elevation could be observed. The $\delta^{34}\text{S}$ values of samples (Table 4) are quite similar to 13.5‰ reported for Lower Cretaceous sea sulfate (Claypool *et al.*, 1980; Cecile *et al.*, 1983). Khademi *et al.* (1997a) and Farpoor *et al.* (2004) also reported that sulfate in Isfahan and Rafsanjan areas, central Iran originates from the Lower Cretaceous sea sulfate. That is why the same origin for soil sulfate in this research is supported.

Table 4. Summary of the sulfur and oxygen isotopic data of some selected sites.

	Mean (‰)	SD (‰)	No. of samples
Sites 6-8			
$\delta^{34}\text{S}$	+11.8	0.23	5
$\delta^{18}\text{O}$	+11.2	0.24	5
Sites 10-14			
$\delta^{34}\text{S}$	+11.9	0.73	4
$\delta^{18}\text{O}$	+11.4	0.73	3
Sites 15-18			
$\delta^{34}\text{S}$	+10.2	1.54	11
$\delta^{18}\text{O}$	+11.1	2.8	10



Gypsum Crystallization Water Geochemistry

The oxygen and hydrogen isotopic composition of the crystallization water of soil gypsum from Isfahan, Rafsanjan and Loot areas, in central Iran, are compared with results of this study in Table 5. The δD and $\delta^{18}O$ values in this study are lighter than the values of the Rafsanjan and heavier than Isfahan and Loot areas.

Since precipitation during cooler temperatures is depleted in heavier isotopes (Craig, 1961; Fontes, 1980; Gat, 1980; Khademi et al., 1997a; Farpoor et al., 2004; and Farpoor and Krouse, 2008), it seems that the study area has experienced a cooler temperature than Rafsanjan area (which is located 120 km west of the studied area) at the time of gypsum crystallization.

Three geochemical processes for gypsum formation have been described by Sofer (1978): oxidation of sulfide minerals, hydration of anhydrite, and direct deposition from an evaporating solution saturated with gypsum. Since the isotopic composition of local meteoric water for this study area was not available, data from Rafsanjan area, which is very similar in climate, was used. Table 6 shows the regression equations between δD and $\delta^{18}O$ values from the study

area as compared with Isfahan and Rafsanjan areas. Because gypsum crystallization water line and the equilibrium line are not parallel to the local meteoric water line (the intercept is at $\delta D = -78.5$ and $\delta^{18}O = -15.5$), oxidation of sulfide minerals could not have played a role in gypsum formation (Sofer, 1978; Dowuona et al., 1992c). On the other hand, gypsum has not been deposited by the hydration of anhydrite because the crystallization water and the mother water lines have not moved along a line with a negative $\Delta\delta D/\Delta\delta^{18}O$ value (Matsubaya and Sakai, 1973; Sofer, 1978). The $\Delta\delta D/\Delta\delta^{18}O$ value in the area is 2.4 and this means that evaporation from a solution saturated with gypsum was the major process for gypsum accumulation in the area. Sofer (1978), Khademi et al. (1997b), and Farpoor et al. (2004) found the $\Delta\delta D/\Delta\delta^{18}O$ values of 2.6, 3.09, and 2.8, respectively, which are similar to the ratio obtained in the present research and could be a further support for the mode of gypsum formation in the area.

CONCLUSIONS

The $\delta^{13}C$ values of soil organic carbon showed an increasing trend toward arid

Table 5. Oxygen and hydrogen isotopic composition (‰, V-SMOW) of the crystallization water of soil gypsum and its mother water in the area studied.

Sample	Crystallization water		Mother water	
	δD	$\delta^{18}O$	δD	$\delta^{18}O$
Site 8 (Byz1)	-47.0	+9.3	-27.6	+5.3
Site 11 (By)	-44.0	+6.4	-24.5	+2.4
Site 11 (Cy)	-52.0	+5.1	-32.6	+1.1
Site 12 (By)	-62.0	+3.4	-42.8	-0.6
Loot area ^a	-82.5	-0.7		
Rafsanjan area (Rock pediments) ^b	-41.9	+6.9		
Rafsanjan area (Mantled pediments) ^b	-36.9	+10.0		
Rafsanjan area (Transitional surfaces) ^b	-28.8	+13.8		
Rafsanjan area (Playa margin) ^b	-8.8	+19.2		
Isfahan area (Mean of colluvial fans) ^c	-68.8	+1.1		
Isfahan area (Mean of plateaus) ^c	-56.5	+4.5		

^a From Farpoor and Krouse (2008).

^b From Farpoor et al. (2004), mean values.

^c From Khademi et al. (1997b).

Table 6. Correlation equations and coefficients (r^2) between δ D and δ 18 O values of gypsum crystallization and meteoric waters.

Water	Correlation equation	r^2
Gypsum crystallization water (Study area)	δ D=2.4 δ 18 O-66	0.77**
Gypsum mother water (Study area)	δ D=2.5 δ 18 O-37	0.77**
Gypsum crystallization water (Rafsanjan) ^a	δ D=2.8 δ 18 O-64.2	0.91**
Meteoric water (Rafsanjan) ^a	δ D=5.9 δ 18 O+16	0.96**
Gypsum crystallization water (Isfahan) ^b	δ D=3.0 δ 18 O-71	0.71**
Global meteoric water ^c	δ D=8.0 δ 18 O+10	ng

^a From Farpoor *et al.* (2004), ^b From Khademi *et al.* (1997b), ^c From Craig (1961), ng: Not given.

** Statistically significant correlation (P< 0.01).

downslope positions of the climotoposequence which is attributed to both the presence of C3 plants under stress and more decomposition of organic matter in lower positions.

The δ 13 C and δ 18 O values of pedogenic carbonates showed a positive correlation ($r=0.6$) in the arid downslope positions. This is probably attributed to the enrichment of both isotopes in the remaining HCO_3^- , during precipitation of CaCO_3 in the system (Salomon and Mook, 1976). However, this correlation ($r= 0.37$) was not observed in the upper landscape positions of the transect with a somewhat Mediterranean climate.

The δ 13 C values of pedogenic carbonates decreased with decreasing elevation. Higher proportion of C3 plants in lower positions and presence of more C4 plants in the upper positions in the past could be considered as possible reasons.

The mean δ 34 S value of the area (11.3‰) is very close to lower Cretaceous sea sulfate (13.5‰) which seems to indicate the sedimentary source of sulfur in the area studied. Mean δ D and δ 18 O values of gypsum crystallization water (-51.2‰ and +6.0‰ respectively) show that direct deposition from an evaporating solution saturated with gypsum is the only possible mechanism of gypsum formation in the area studied.

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REFERENCES

1. Boutton, T. W. 1991. Stable Isotope Carbon Ratios of Natural Materials. I. Sample Preparation and Mass Spectrometer Analysis. In: "*Carbon Isotope Techniques*", (Eds.): Coleman, D. C. and Fry, B.. Academic Press San Diego, PP. 155-172 .
2. Boutton, T. W. 1996. Stable Isotope Ratios of Soil Organic Matter and Their Use as Indicators of Vegetation and Climate Change. In: "*Mass Spectrometry of Soils*", (Eds.): Boutton, T. W. and Yamasaki, S.. Marcel Dekker Inc., New York, PP. 47-81.
3. Cecile, M. P., Shakur, M. A. and Krouse, H. R. 1983. The Isotopic Composition of Western Canadian Barites and the Possible Derivation of Oceanic Sulphate δ 34 S and δ 18 O Age Curves. *Can. J. Earth Sci.*, **20**: 1528-1535.
4. Cerling, T. E. and Hay, R. 1986. An Isotopic Study of Paleosol Carbonates from Olduvai Gorge. *Quat. Res.*, **25**: 63-78.



5. Cerling, T. E. and Quade, J. 1993. Stable Carbon and Oxygen Isotopes in Soil Carbonates. In: "*Climate Change in Continental Isotope Records*", (Eds.): Swart, P. K., Lohmann, K. C., McKenzie, J. and Savin, S.. *Geophys. Monogr.* **78**: 217-231.
6. Claypool, G. E., Holser, W. T., Kaplan, I. R., Sakai, H. and Zak, I. 1980. The Age Curves of Sulfur and Oxygen Isotopes in Marine Sulfate and Their Mutual Interpretation. *Chem. Geol.*, **28**: 199-260.
7. Coleman, M. C., Shepherd, T. J., Durham, J. J., Rouse, J. D. and Moore, G. R. 1982. Reduction of Water with Zinc for Hydrogen Isotope Analysis. *Anal. Chem.*, **54**: 993-995.
8. Craig, H. 1961. Isotopic Variations in Meteoric Waters. *Sci.*, **133**: 1702-1703.
9. Delucia, E. H., Schlesinger, W. H. and Billings, W. D. 1988. Water Relations and the Maintenance of Sierran Conifers on Hydrothermally Altered Rock. *Ecology*, **9**: 303-311.
10. Dowuouna, G. N., Mermut, A. R. and Krouse, H. R. 1992a. Isotopic Composition of Salt Crusts in Saskatchewan, Canada. *Chem Geol.*, **94**: 205-213.
11. Dowuouna, G. N., Mermut, A. R. and Krouse, H. R. 1992b. Stable Isotopes of Salts in Some Acid Sulfate Soils of North America. *Soil Sci. Soc. Am. J.*, **56**: 1646-1653.
12. Dowuouna, G. N., Mermut, A. R. and Krouse, H. R. 1992c. Isotopic Composition of Hydration Water in Gypsum and Hydroxyl in Jarosite. *Soil Sci. Soc. Am. J.*, **56**: 309-313.
13. Ehleringer, J. R., Field, C. B., Lin, Z. F. and Kuo, C. Y. 1986. Leaf Carbon Isotope and Mineral Composition in Subtropical Plants along an Irradiance Cline. *Oecologia*, **70**: 520-526.
14. Ehleringer, J. R., Sage, R. F., Flanagan, L. B. and Pearcy, R. W. 1991. Climate Change and the Evolution of C4 Photosynthesis. *Trends Evolutionary Ecol.*, **6**: 95-97.
15. Epstein, S. and Mayeda, T. 1953. Variation of $\delta^{18}\text{O}$ Content of Waters from Natural Sources. *Geochim. Cosmochim. Acta*, **4**: 213-224.
16. Farpoor, M. H., Khademi, H., Eghbal, M. K. and Krouse, H. R. 2004. Mode of Gypsum Deposition in Southeastern Iranian Soils as Revealed by Isotopic Composition of Crystallization Water. *Geoderma*, **121**: 233-242.
17. Farpoor, M. H. and Krouse, H. R. 2008. Stable Isotope Geochemistry of Sulfur Bearing Minerals and Clay Mineralogy of Some Soils and Sediments in Loot Desert, Central Iran. *Geoderma*, **146**: 283-290.
18. Fontes, J. Ch. 1980. Environmental Isotopes in Groundwater Hydrology. In: "*Handbook of Environmental Isotope Geochemistry*", (Eds.): Fritz, P. and Fontes, J. Ch.. Elsevier, Amsterdam, *The Terrestrial Environment*, **1**: 75-140.
19. Gat, J. R. 1980. The Isotopes of Hydrogen and Oxygen in Precipitation. In: "*Handbook of Environmental Isotope Geochemistry*", (Eds.): Fritz, P. and Fontes, J. Ch.. Elsevier, Amsterdam, *The Terrestrial Environment*, **1**: 21-47.
20. Gonfiantini, R. and Fontes, J. C. 1963. Oxygen Isotope Fractionation in the Water of Crystallization of Gypsum. *Nature (Lond.)*, **200**: 644-646.
21. Halas, S. and Krouse, H. R. 1982. Isotopic Abundances of Water of Crystallization of Gypsum from the Miocene Evaporate Formation, Carpathian Foredeep, Poland. *Geochim. Cosmochim. Acta*, **46**: 293-296.
22. Khademi, H. and Mermut, A. R. 1999. Submicroscopy and Stable Isotope Geochemistry of Carbonates and Associated Palygorskite in Iranian Aridisols. *European J. Soil Sci.*, **50**: 207-216.
23. Khademi, H., Mermut, A. R. and Krouse, H. R. 1997a. Sulfur Isotope Geochemistry of Gypsiferous Aridisols from Central Iran. *Geoderma*, **80**: 195-209.
24. Khademi, H., Mermut, A. R. and Krouse, H. R. 1997b. Isotopic Composition of Gypsum Hydration Water in Selected Landforms from Central Iran. *Geoderma*, **138**: 245-255.
25. Landi, A., Mermut, A. R. and Anderson, D. W. 2003. Origin and Rate of Pedogenic Carbonate Accumulation in Saskatchewan Soils, Canada. *Geoderma*, **117**: 143-156.
26. Matsubaya, O. and Sakai, H. 1973. Oxygen and Hydrogen Isotopic Study on the Water of Crystallization of Gypsum from the Kuroko Type Mineralization. *Geoderma*, **7**: 153-165.

27. Mermut, A. R., Amundson, R. and Cerling, T. E. 2000. The Use of Stable Isotopes in Studying Carbonate Dynamics in Soils. In: "*Global Climate Change and Pedogenic Carbonates*", (Eds.): Lal, R., Kimble, J. M., Eswaran, H., Stewart, B. A.. Lewis Publishers, Washington DC, PP. 65-85.
28. Mermut, A. R. and Arshad, M. A. 1987. Significance of Sulfide Oxidation in Soil Salinization in Southern Saskatchewan, Canada. *Soil Sci. Soc. Am. J.*, **51**: 247-251.
29. Monger, H. C., Cole, D. R., Gish, G. W. and Giordano, T. H. 1998. Stable Carbon and Oxygen Isotopes in Quaternary Soil Carbonates as Indicators of Ecogeomorphic Changes in the Northern Chihuahuan Desert, USA. *Geoderma*, **82**: 137-172.
30. Nettleton, W. D. (Ed.) 1991. Occurrence, Characteristics, and Genesis of Carbonate, Gypsum, and Silica Accumulations in Soils. SSSA Spec. Publ., **26**: 149.
31. Nordt, L. C., Wilding, L. P., Halmark, C. T. and Jacob, J. S. 1996. Stable Carbon Isotope Composition of Pedogenic Carbonates and Their Use in Studying Pedogenesis. In: "Mass Spectrometry of Soils", (Eds.): Boutton, T. W. and Yamasaki, S.. Marcel Dekker Inc., New York, PP.133-154.
32. O'Leary, M. H. 1988. Carbon Isotopes in Photosynthesis. *Bioscience*, **38**: 328-336.
33. Pradhananga, T. M. and Matsuo, S. 1985. D/H Fractionation in Sulfate Hydrate-water Systems. *J. Phys. Chem.*, **89**: 1869-1872.
34. Roether, W. 1970. Water-CO₂ Exchange Set-up for the Routine $\delta^{18}\text{O}$ Oxygen Assay of Natural Waters. *Int. J. Appl. Radiat. Isot.*, **21**: 379-387.
35. Romanek, C. S., Grossman, E. L. and Morse, J. W. 1992. Carbon Isotope Fractionation in Synthetic Aragonite and Calcite: Effects of Temperature and Precipitation Rate. *Geochim. Cosmochim. Acta*, **56**: 419-430.
36. Salehi, M. H., Khademi, H., Eghbal, M. K. and Mermut, A. R. 2004. Stable Isotope Geochemistry of Carbonates and Organic Carbon in Selected Soils from Chaharmahal Bakhtiari Province, Iran. *Commun. Soil Sci. Plant Anal.*, **35**: 1681-1697.
37. Salomons, W. and Mook, W. G. 1976. Isotope Geochemistry of Carbonate Dissolution and Reprecipitation in Soils. *Soil Sci.*, **122**: 15-24.
38. Schlesinger, W. H., Marion, G. M. and Fonteyn, P. J. 1989. Stable Isotope Ratios and the Dynamics of Caliche in Desert Soils. In: "Stable Isotopes in Ecological Research", (Eds.): Rundel, P. W., Ehleringer, J. R. and Nagy, K.. Springer-Verlag, Berlin, PP. 309-317.
39. Sofer, Z. 1978. Isotopic Composition of Hydration Water in Gypsum. *Geochim. Cosmochim. Acta*, **42**: 1141-1149.
40. Soil Survey Staff, 2010. *Keys to Soil Taxonomy*. United States Department of Agriculture, Natural Resources Conservation Service, USA, 338 PP.
41. Stevenson, B. A., Kelly, E. F., McDonald, E. V. and Busacca, A. J. 2005. The Stable Carbon Isotope Composition of Soil Organic Carbon and Pedogenic Carbonates along a Bioclimatic Gradient in the Palouse Region, Washington State, USA. *Geoderma*, **124**: 37-47.
42. Toomanian, N., Jalalian, A. and Eghbal, M. K. 2001. Genesis of Gypsum Enriched Soils in North-west Isfahan, Iran. *Geoderma*, **99**: 199-224.
43. Volkoff, B. and Cerri, C. C. 1987. Carbon Isotope Fractionation in Subtropical Brazilian Grassland Soils: Comparison with Tropical Forest Soils. *Plant Soil*, **102**: 27-31.



ژئوشیمی ایزوتوپ‌های کربن، اکسیژن و گوگرد در خاکهای واقع بر ردیف اقلیمی-توپوگرافی در استان کرمان، ایران مرکزی

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چکیده

داده‌های ایزوتوپی کربن و اکسیژن به فهم بهتر شرایط محیطی زمان تشکیل خاک کمک می‌نمایند. خاکهای ۱۸ محل نمونه‌برداری در طول یک ردیف پستی بلندی-اقلیمی از ارتفاعات لاله زار (با ارتفاع ۴۳۵۱ متر از سطح دریا و رژیم رطوبتی-حرارتی زیریک-مزیک) تا حوضچه پست شهداد (با ارتفاع ۲۵۰ متر از سطح دریا و رژیم رطوبتی-حرارتی ارید-هایپرترمیک) در استان کرمان واقع در ایران مرکزی مورد مطالعه قرار گرفتند. مقادیر $\delta^{13}\text{C}$ مربوط به کربن آلی خاک از $-20/6$ پرمیل تا $26/9$ - پرمیل (PDB) تغییر یافت. مقادیر $\delta^{13}\text{C}$ مربوط به کربنات‌های خاکساز از $-2/2$ تا $2/2$ + پرمیل تغییر یافت و به طرف پایین شیب با روند کاهشی روبرو بود. در بخشهای ارید پایین شیب در زمین نما یک همبستگی مثبت ($r=0/6$) بین $\delta^{13}\text{C}$ و $\delta^{18}\text{O}$ یافت شد در حالیکه ارتباط متفاوتی ($r=0/37$) در موقعیت‌های بالای شیب با اقلیم مدیترانه‌ای به دست آمد. به نظر می‌رسد که در موقعیت‌های پایین زمین‌نما، مقادیر بیشتری از گیاهان با مسیر فتوسنتزی C3 تحت تنش خشکی وجود داشته و نیز تجزیه بیشتر ماده آلی صورت پذیرفته باشد. مقادیر $\delta^{13}\text{C}$ موجود در کربن آلی و نیز کربنات‌های خاکساز و نیز روند تغییرات آنها در طول توالی نشان داد که مقدار بیشتری از گیاهان C3 در موقعیت‌های پایینی زمین‌نما و مقادیر بیشتر از گیاهان C4 در تاریخچه بخش‌های فوقانی منطقه وجود داشته است. میانگین $11/3$ پرمیل مربوط به $\delta^{34}\text{S}$ نشان داد که سولفات با منشاء دریایی مربوط به کرتاسه پایینی به عنوان منبع گوگرد در منطقه می‌باشد. میانگین $-51/2$ و $+6/0$ پرمیل مربوط به δD و $\delta^{18}\text{O}$ در آب شبکه بلوری گچ حاکی از آن است که رسوب مستقیم از محلول اشباع از گچ به عنوان تنها سازوکار تشکیل این کانی در منطقه به حساب می‌آید.