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## Changes in particle sizes and geochemistry of Siyah Keshim lagoon sediment of Gilan province to determine origin and tectonic position of sediment

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Abstract. Useful information was obtained about the environmental condition of this region such as energy, sediment location, origin, sediment carrying path, pond evolutionary process, and tectonic conditions and origins of sediments by studying physical and geochemical sediment changes processes in place and time, distribution of sediments and

elements in lagoon bed, and also identification the effective factors on sediment distribution model. In this regard, 59 sediment samples were taken from Siyah Keshim lagoon and were analyzed chemically and aggregation by XRF and ICP-MS technic. Adaptation of data by Folk diagrams showed that this region is placed in a range of sand, muddy sand, sand with a little gravel, muddy sand with a little gravel, and silty sand. Weak to medium sorting and negative tilting shows sediment in a coastal area. Geochemical evidence shows that SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio in these sediments is 2.6-3.7. In addition, Na<sub>2</sub>O value shows relatively low sediment investigation for sediments of this lagoon. Moreover, determination of the weathering effect in origin place by the chemical index of alteration (CIA) and chemical weathering index (CWI) shows intensive chemical alternation on sediments. Index of combined variety was averagely 1.54 in the studied sediments and show that sediments resulted from the first cycle sediment. Using tectonic separating diagrams based on the primary and secondary oxidants percentage show the sediments are related to subduction margin.

Key words: Siyah Keshim, lagoon, sorting, sediment, geochemistry

## Використання змін розмірів частинок та геохімії осадів лагуни Сія Кешим провінції Гілан для визначення походження та тектонічного положення осадів

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Анотація. Отримано корисну інформацію про стан навколишнього середовища дослідженого регіону, зокрема щодо енергії, поширення осадів, їх походження, шляхів переносу відкладів, процесу еволюції водоймища, тектонічних умов та походження відкладів шляхом вивчення фізичних та геохімічних процесів зміни осадів у місці та часі, розподілу відкладів та елементів у річищі лагуни, а також виявлення ефективних факторів на моделі розподілу осадів. Для цього із лагуни Сія Кешим було взято 59 зразків осаду, які були проаналізовані хімічно та агрегатно за допомогою техніки XRF та ICP-MS. Адаптація даних за діаграмами Фолка показала, що ця область розміщена в діапазоні піску, мулистого піску, піску з невеликою кількістю гравію та мулистого піску. Від слабкого до середнього сортування та негативний нахил свідчить, що осад формувався у прибережній зоні. Геохімічні дані показують, що співвідношення SiO<sub>2</sub> / Al<sub>2</sub>O<sub>3</sub> у цих відкладах становить 2,6-3,7. Крім того, значення Na<sub>2</sub>O свідчить про відносно низьке дослідження осадів для відкладів цієї лагуни. Більше того, визначення ефекту звітрювання в місці походження за хімічним індексом зміни (CIA) та індексом хімічного звітрювання (CWI) показує інтенсивне хімічне змінення відкладів. Індекс комбінованого різноманіття становить у середньому 1,54 у досліджуваних відкладах і показує, що відклади були результатом осаду першого циклу. Використовуючи тектонічні розділові діаграми на основі процентного вмісту первинних та вторинних окисників, можна побачити наявність осадів на ділянці активного континенту (ACM), дузі континент-острів (CIA) та острівній океанічній дузі (OIA) та показує, що дослідженні оказує, що дослідженні відклади в на всодів на ділянці активного континенту (ACM), дузі континент-острів (CIA) та острівній океанічній дузі (OIA) та показує, що дослідженні відклади пов'язані із субдукційною границею.

Ключові слова: Сія Кешим, лагуна, сортування, осад, геохімія

Introduction. Lagoons have many advantages for having hydrological characteristics. Lagoons not only supply a part of underground waters, but also provide an environment as the best ecosystem to supply many birds and aquatics foods (Nuri, 2009). In addition, lagoon prevents penetration of salty waters and floods prevalence by setting water flow and has a significant role in preventing dessert (Nuri, 2009). In addition to the mentioned cases, lagoons have a significant role in preventing erosion of coastal lines, stabilization of the region's air based on rainfall and ambient temperature, livestock feed, agricultural usages, minerals extraction such as potassium and phosphorus, and air purification of adjacent areas, etc. (Mohammadi et al., 2012). Anzali lagoon is one of the international protected lagoons that were studied by researchers (Amini Ranjbar, 1998; Riyahi et al, 2005, Sharifi, 2006). This lagoon is an ecosystem of many endangered species and has a more effective role in preventing flood and acts such as sediment traps (Kazanci et al, 2004).

Anzali lagoon was made because of coastal sediment growth as coastal tabs and dams. The expansion of sand stripe masses separated a part of coastal waters that finally formed coastal back lakes after enclosure. Alzali lagoon is one of these coastal back lakes that formed a part of Caspian Sea coastal waters in the past. This lagoon developed a lot in the past but was filled gradually by alluvial-delta sediment of Sefidrud branches and rivers of Rasht, Fuman and Masal region. Anzali lagoon is the tectonic resulted lethargy that became separated from Caspian seawater recession and formed by the sand blade (the area between Anzali and Kapurchal) caused by sea movements and its waves (Ranjbar, 2012).

Siyah Keshim area that is in the southwest of lagoon has the average depth of 1m and us mostly covered by vegetable plants, especially reed, Cattail, and Azolla. The relationship between Anzali lagoon and Siyah Keshim area is possible through the narrow strait in its northeast (Mohammadi et al., 2005).

Sediment granulation is used as the most principal and important characteristics of sediment particles to discern and analyze particle size and classification of sediment environment, sediment origin, transmission history, and erosion conditions (Bui et al, 1990; Folk & Ward, 1957; Friedman, 1979).

Since the sediment particles are in varied sizes and can be observed in various sizes, their granulation is based on their highest diameter that was produced by Adon and Wentworth for the first time. Wentworth scale is a logarithmic scale in which each grade is twice bigger than the next smaller grade. Phi scale is shown by  $\Phi$  is the changed form of Wentworth scale that was invented by Chrombin in 1937, and scaling boundaries must change to  $\Phi$  values.

 $\Phi = -\log 2d$ 

where d – particle diameter (mm)

Sediment was geochemically studied in the next step to fill and confirm the obtained information from granulation. Using the geochemical element to determine the old environment conditions is significantly important, and distribution of the main and secondary elements in sediment depends on mineralogical composition, temperature, fluid composition, oxidation, and reduction conditions (Adabi, 2004). Studies show that elements amounts and compositions are sensitive to environmental conditions, sai. Analysis of the main (Mg, Ca) and secondary (Sr, Mn, Na, Fe) elements of sediments open a way of understanding sedimentary environmental time by indicating their dispersion and distribution. The element geochemistry for the present elements in each sample is a good guidance for climate changes because some elements in the soil are sensitive to environmental conditions in a way that some elements report the certain conditions; for example, high amounts of Fe, Mn shows reduction environment, (Nekukhu, 2003). The elements geochemistry can show temperature and raining conditions well. Elements of Mn, Sr, Mn replace with elements such as Ca under the specific climate conditions in crystal network. Changes in Mg/Ca, Sr/ Ca, Mg/Ca ratios along cores show changes in lake conditions chronically (Taghavi et al., 2013).

Methods and materials. *Geographical conditions and geometry of the studied region*. Siyah Keshim lagoon of Gilan province (Fig. 1) is limited to Anzali city from north to Sowme'eh Sara city from south, to Rasht city from east, and to Kapurchal and Anzali waterfront from the west.

Based on the geographical map studies of Bandar-e Anzali in 1: 100000 from publications of Geological Survey & Mineral Explorations of Iran (GSI) Tehran (Khabaznia et al., 2005) of Anzali lagoon region contains rocks of Paleozoic and Caucasian periods and has specific characteristics, but Siyah Keshim lagoon is very new geologically and its creation can be known for about 7 centuries ago.

The altitudes of the catchment area of this wetland are related to Cretaceous to Jurassic courses and also the third period in the context of limestone, conglomerate, and sandstone. Based on the structural geology of the studied region, a resulted face of the earth performance shear-stress structure is made by the rock of diatomaceous deposits from the Paleozoic era and other sedimentary deposits and Azar Caves



Fig. 1 The geographical condition of the studied region

related to the Mesozoic era. Strain-slip faults are one of the most vivid structural element seen in this region. Anticlines and syntaxes in the north-east axis of the Southwest were seen in the southwest of the studied region that changes in center and northwest to west-east and northwest-southeast line. Most of these buildings were unidirectional and classified in conical faults, Aghanabati, (2006).

**Sampling methods and data analysis.** Sampling was conducted in August 2016. Therefore, two stations were selected in various lagoons parts (Fig. 3). And the sedimentary cores were conducted in the Egher machine in the sediment of the lagoon. Thus, the first core section had 675cm depth with 34 samples and the second core section had 486cm depth with 25 samples (Fig. 2).

Samples were transferred to the laboratory to prepare for granulation, studying sedimentary characteristics, mineralogy nature, determination of the major and trace elements. After hydrometric tests, the related calculations to correct data were conducted by calculating laboratory temperature and silt and clay weight percentages were obtained (Feyznia, 2008).

To calculate these parameters, first, the accumulative frequency diagrams of each sample were drawn after performing granulometric tests by Gradistat and Excel software. Then, total skewness index (SKI) and total standard deviation index (SDI), mean (Mz), kurtosis (KU) was calculated as following using relations Folk (1980) and Ward (1957) using values of Ø84, Ø75, Ø50, Ø25, Ø16, Ø5. Since these diameters are based on mm and the obtained formula for statistical parameters are based on  $\phi$ , the related percentage diameters changed from mm to  $\phi$  and then were inserted in formulas (Table 1).

These samples were sent to calculate the major elements (Mg, Ca) and secondary (Sr, Mn, Na, Fe) to Geochemical Laboratory of Geological Survey of



Fig. 2 1st and 2nd cutting sedimentary column of the studied region

able	1.	Sedimenta	ry	parameters	and	the	related	l re	lati	ons	were	tes	ted	fo	r geoc	hemical	stuc	lies
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index	mean diameter	sorting	skewness	kurtosis		
formula	$M_Z = \frac{\phi_{16} + \phi_{50} + \phi_{84}}{3}$	$\sigma_I = \frac{\phi_{84} - \phi_{16}}{4} + \frac{\phi_{95} - \phi_5}{6 \cdot 6}$	$Sk_{I} = \frac{\phi_{16} + \phi_{84} - 2\phi_{50}}{2(\phi_{84} - \phi_{16})} + \frac{\phi_{5} + \phi_{95} - 2\phi_{50}}{2(\phi_{95} - \phi_{5})}$	$K_G = \frac{\phi_{95} - \phi_5}{2.44(\phi_{75} - \phi_{25})}$		

Iran. The range of the major element (Mg, Ca) and secondary ones (Sr, Mn, Na, Fe) was calculated mg/g by OES, XRF ICP-MS, ICP- methods. Plots of major oxides and sub-elements on different diagrams (Basu et al., 1975; Bhatia., 1983); Dickinson et al., 1983; Roser and Korsch., 1986; Bhatia and Crook., 1986); Suttner and Duta., 1986) helped to obtain the related results to the origin, tectonic position, and climatic conditions of these sediments.

**Discussion and conclusion.** Folk diagrams (1954) were used to determine the name of sediments of this region based on their constitutional particles that showed the sediments of this region were placed around sand, mud sands, gravel sand with slightly muddy sandstone, and silty sand (Fig. 3).

Based on the obtained information from the statistical calculation, and the related tables and diagrams using Excel and Gradistat indicated that sediment sorting of this area is 0.7-1.9, sediment kurtosis is 0.1-0.3, and kurtosis is in 0.6-0.9 (Folk, 1980).

The sediments of this area are wide based on kurtosis, negative skewness (toward big particles), and medium to bad sorting (Feyznia, 2008). The

Sand Clavey Muddy Silty Sand 509 Sandy Mud Sandy Clay Silt Mud Clay Silt 1:2 SiltClay Ratio 2.1

Fig. 3 Sediment based on its constitutional particles (folk, 1954)

previous studies on this lagoon confirmed this fact that the sediments of this area are medium to tiny particles (Sabzivala et al., 2011).

Determination of tectonic position of sediments

based on geochemistry of the major elements. The tectonic position has two characteristics of studying the origin places including continental blocks, volcanic arc system, and collision belts and examining the boundary type among sheets including rift or inactive continental margins, active or orogeny continental margins, or striped fault margins (Dickinson and Suczek ,1979; Dickinson et al, 1983; Garzanti et al, 2003; Garzanti et al, 2007).

The similar results were obtained in the determination of sediments tectonic position by drawing Rusar and Kurosh tectonic separating diagrams (Roser and Korsch., 1986) and 2d and Bhatia functional separating diagrams (Bhatia, 1983) (Fig. 4&5).

These diagrams based on the logarithmic ratio of  $K_2O/Na_2O$  versus SiO<sub>2</sub> percent (Fig. 4) and TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> values versus Fe<sub>2</sub>O<sub>3</sub>+MgO were drawn. Their formation in Arctic islands is confirmed for sedimentary samples. As it is observed in these diagrams, it can be claimed that TiO<sub>2</sub> and total values of Al<sub>2</sub>O<sub>3</sub>+Fe<sub>2</sub>O<sub>3</sub>+MgO in arctic islands reduced to inactive margins (Fig. 6).



Determination of the tectonic rank of sediments based on the geochemistry of the secondary elements

Changes in secondary elements in clastic rocks are in low weathering and diagenetic conditions Roser and Korsch, 1986



Fig. 4 Tectonic separating diagrams of sediments based on K<sub>2</sub>O/Na<sub>2</sub>O versus SiO<sub>2</sub> percent logarithmic ratio.



Fig. 5 Tectonic separating diagrams of sediments based on Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> percent versus Fe<sub>2</sub>O<sub>3</sub>+Mgo logarithmic ratio

(McLennan et al., 1993). Therefore, the secondary elements are significantly mentioned in the determination of tectonic origin and place (Bhatia and Crook., 1986; McLennan., 2001; Eriksson et al., 1994) which cause many studies on the present secondary elements in the sedimentary rocks to determine the tectonic position and their origin (Bahlburg., 1998); Burnett and Quirk., 2001; McLennan et al., 1993; Zimmermann and Bahlbarg., 2003).

Therefore, 3d diagrams for the secondary elements

were drawn to determine the tectonic position and the obtained results of them in confirmation the resulted diagrams for the major elements showed that the tectonic position of Quaternary sediments of Siyah Keshim lagoon is an arctic continental island (Fig. 7). The related area to the firmed sediments in active and inactive continental margins was overlapped in the La-Th-Sc 3d drawing, while these two environments are completely separated in Th-Sc-Zr/10 3d drawing (Fig.7) (Adabi, 2004).



Fig. 6 Tectonic separating diagrams of sediments based on TiO<sub>2</sub> percent versus Fe<sub>2</sub>O<sub>3</sub>+MgO logarithmic ratio.

Based on drawing the paired Ti/Zr elements versus La/Sc that is shown in Fig. 8, sediments tectonic position in Suyah Keshim area of Gilan province shows arctic continental margin (ACM) and arctic continental island (CIA). Moreover, the mentioned rocks tectonic environments by diagram (Schandl & Gorton, 2002) are shown in Fig. 9 and 10 based on the secondary elements. All the studied samples are around ACM based on this diagram.

The determined areas include A: oceanic arctic islands, B: arctic continental island, C: active continental margin, D: inactive margins

Based on the obtained results from drawing the high geochemical diagrams based on the oxidants percentage of the major and secondary elements that show the tectonic position of this region sediments of continental and oceanic arctic island, continental active margin, and inactive continental margin. It can be concluded based on citing studies (Asiabanha & Foden, 2012) that the related studied sediments are related to subduction margin.

**Interpretation of origin area weathering.** The mobility of the major elements during weathering, transportation, and processes after sediment can be used to determine the chemical maturity of sediments, (McLennan et al., 1993).

The very low concentration of Na<sub>2</sub>O in sediments shows high sedimentary maturity (Fig. 11). Moreover, SiO<sub>2</sub> /Al<sub>2</sub>O<sub>3</sub> ratio is the usable index to determine sediment maturity (Potter, 1978). SiO<sub>2</sub> /Al<sub>2</sub>O<sub>3</sub> ratio higher than 5-6 in sedimentary rocks show their high sedimentary maturity (Roser et al., 1996). SiO<sub>2</sub> /Al<sub>2</sub>O<sub>3</sub>



Fig. 7 Tectonic separating diagram of sediments based on the secondary elements frequency (Bhatia & Crook, 1986)



Fig. 8 Tectonic separating diagram based on Ti/Zr versus La/Sc ratio for the studied samples (Bhatia & Crook, 1986)



Fig. 9 The diagram of tectonic environment determination based on Th/Ta versus Yb ratio (Schandl & Gorton, 2002)



Fig. 10 The diagram of tectonic environment determination based on Th/Hf versus Ta/Hf (Schandl & Gorton, 2002)

ratio in samples is varied in 2.6-3.7. These numbers show relatively low maturity in the studied region sediments.

from the following formula:

ICV=(Fe<sub>2</sub>O<sub>3</sub>+K<sub>2</sub>O +Na<sub>2</sub>O +CaO+MgO+MnO+TiO<sub>2</sub>)/Al<sub>2</sub>O<sub>3</sub>

ICV combined variety can be used to determine the first cycle sediment or the obtained sediments from the second cycle (Cox et al., 1995) that is obtained

Samples with higher ICV than 1 are probably for the first cycle sediments, and which with smaller

ICV than 1 may be from the second cycle sediments or the severely weathered sediments from the first cycle sediments (Cullers & Podkovyrov, 2002). The calculated values from ICV in quaternary sediments of this region are 0.9-5.35 with an average of 1.54. Thus, it can be stated that the most sediments of the studied lagoon are related to the first cycle sediments.

Weathering history of the clastic rocks is mostly estimated by calculating the mobile oxides ratio of  $K_2O$ ,  $Na_2O$ , and CaO than non-mobile oxide  $Al_2O_3$ (Nesbitt & Young, 1982). The most used index in this formula is alternation chemical index (Nesbitt & Young, 1982). This index is obtained by the following relation and oxides in it was stated in mole.

## $CIA=[Al_2O_3/Al_2O_3+CaO+Na_2O+K_2O]\times 100$

CaO is the present calcium in rock silicate components, and this value must be modified in samples that high CaO is related to diagenesis cement. CIA range may be low, medium, and high varied from 50 to 100. Increasing CIA from down to up is related to alternation chemical degree. Low CIA shows no alternation or very low alternation and is a reflection of cold and dry climate conditions, while medium and high CIA with mobile cations transmission such as (K+, Na+, Ca<sub>2</sub>+) and remaining the constituters (Ti<sub>4</sub>+ and Al<sub>3</sub>+) is related to less mobility (Nesbitt & Young, 1982). Samples were considered with higher CaO than 5% to determine CIA precisely and CaO removal from carbonate cement (Batumike et al., 2006, Nesbitt, 2003, Garcia et al., 2004). The calculated CIA for the studied samples was 0.78-63 and is 72 averagely in samples which show severe chemical alternation in sediments. Chemical index of weathering (CIW) is extensively used to determined rock weathering degree and is obtained by the following formul (Harnois, 1988).

$$CIW = [Al_2O_3/Al_2O_3 + CaO + Na_2O] \times 100$$

The mean of this index for the sediments of Siyah Keshim area is 80.73. Using CIA and CIW indexes in samples with high CaO changes doesn't show interesting results (Cullers, 2000). In this regard (Cullers, 2000), another weathering index can be offered for samples with high CaO. This index is stated as follows:

$$CWI' = [(Al_2O_3/Al_2O_3 + Na_2O)] \times 100$$

In which, oxides are considered in molecular ratio. The mean of this index in the studied samples is 95.47 that show the severe weathering of these samples.

This result was obtained finally based on the calculated indexes in which the sediments of Siyah Keshim area is for the first sedimentary cycle with relatively low sedimentary maturity, and has severe chemical weathering on then and alternate them.

**Conclusions.** Sediments are considered as data in environmental studies and its conditions are the most important evidence particularly in the previous environmental conditions. Many other pieces of



Fig. 11 Drawing Na,O versus K,O

evidence such as paleontology, botanical, and biological effects generally and even hum civilization effects are evaluated by sedimentary data.

In other words, the real history of the earth and its conditions are hidden in the body of the earth sediments. Sediments can be examined through various views such as particles size and diameter, ration of the formed particles of a sediment, sorting, particles kurtosis, skewness, rounding, and some other statistical parameters such as mean, mode, standard deviation, etc. each of these cases shows genre, origin, and environmental conditions that formed sediments.

Studying quaternary sediments for two studied sections of Siyah Keshim lagoon in Gilan province showed that this area has a sandy texture, mud sands, sand with slightly gravel, sandy mud with slightly gravel, and silty sand through sedimentology view. Sediments sorting are medium to weak, negative skewness, and many big particles and plate kurtic through kurtosis view which show sediment in the coastal area. Regarding the obtained results from drawing the geochemical diagrams based on the major and secondary elements oxides, it can be concluded that the studied sediments are related to a subduction margin. Moreover, geochemical evidence shows that SiO<sub>2</sub>/Al<sub>2</sub>O<sub>2</sub> ratio in these sediments is 2.6-3.7 and also Na<sub>2</sub>O has the relatively low sedimentary maturity for the sediments of this lagoon. The mean coefficient weathering indexes such as ICV, CIW, CWI, and CIA also show that the mentioned sediments are mainly related to the first sediment cycle and tolerate high chemical weathering.

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