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Rb-Sr AND Sm-Nd ISOTOPES STUDY OF SERPENTINITES AND THEIR IMPACT ON THE TECTONIC SETTING OF ZAGROS SUTURE ZONE, NE IRAQ

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ABSTRACT

In an attempt to establish a chronology for serpentinite rocks, from various areas along the line of the Zagros Suture Zone (NE Iraq), Sr-Nd isotopic studies have been carried out on selected samples collected from an association of ophiolite suite and ophiolitic mélange samples. Sr model ages of (80 – 110) Ma for three ophiolite suite samples are concordant with previous K-Ar ages of (97 – 118) Ma and may indicate ophiolite formation and/ or serpentinization above an intra-oceanic suprasubduction zone of island-arc affinity (fore-arc) during the Albian – Cenomanian. A profound Rb-Sr age variation of (150 – 770) Ma is due to the effect of mélange phenomenon on ophiolitic serpentinites (imbricate), tectonically associated with intraoceanic suprasubduction zone (~ Late Maastrichtian) of Walash volcano – sedimentary sequence of island-arc affinity. The **Sr** and **εNd** isotopic composition suggests that the source of serpentinite is enriched-upper mantle, which with time had developed an isotopic heterogeneity. The probable age of emplacement of serpentinites associated with ophiolite massif was ~ 30 Ma, while ophiolitic mélange serpentinites were emplaced post Paleocene – Eocene.

دراسة نظائر الربيديوم – السترونتيوم والسماريوم – النيديميوم لصخور السربنتينايت وتأثيرها على الوضع التكتوني لنطاق ملتحم زاكروس، شمال شرق العراق

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المستخلص

تم اختيار نماذج من مناطق مختلفة على طول خط نطاق ملتحم (درز) زاكروس (شمال شرق العراق) لتحديد أعمار صخور السربنتينايت. إن موديل العمر النموذجي للسترونتيوم من الصخور المرتبطة بمعية الأفيولايت تتراوح بين (80 - 110) مليون سنة المتناغم مع العمر المحسوب سابقا بطريقة البوتاسيوم – الأركون (97 – 118 مليون سنة) والذي يؤكد تكون الأفيولايت وعملية السربنتنة المرتبطة به وفي بيئة تكتونية فوق نطاق الغوران ضمن المحيط (مقدمة القوس البركاني) خلال الألبيان – السينومينيان. هنالك تباين واضح في أعمار الربيديوم – السترونتيوم من (150 – 770) مليون سنة في صخور سربنتينايت الميلانج، والذي يعكس تأثير ظاهرة الميلانج على السربنتينايت الأفيولايتي (المتداخل) والمرتبط بالقوس البركاني فوق نطاق الغوران المحيطي الذي نتج عنه تكون تعاقبات صخور والاش البركانية – الرسوبية في نهاية الماسترختيان. يشير التركيب النظائري للسترونتيوم والنيديميوم أن مصدر السربنتينايت يمكن إرجاعه الى جبة عليا غنية عانت من تغيير في التراكيب مع مرور الزمن نتيجة لتأثير ظاهرة الميلانج. أن عمر التموضع المتوقع للسربنتينايت المرافق لكتلة الأفيولايت هو بحدود 30 مليون سنة، بينما تموضع السربنتنايت الميلانجي بعد الباليوسين – الأيوسين.

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INTRODUCTION

The Zagros Suture Zone (ZSZ), which was formed as a result of a collision between the Arabian passive margin and the Iranian microcontinent active margin, is characterized by tectonic units of thrust sheets, which crop out in a (5 – 7) Km wide belt along the Iraqi – Iranian borders (Fig.1). The tectonic units (zones) comprise from the outer part of the Suture Zone inwards: Qulqula – Khwakurk, Penjween – Walash, and Shalair, which were emplaced during Late Cretaceous and Late Tertiary thrusting (Aswad, 1999 and Jassim *et al*., 2006). Furthermore, ZSZ is distinguished by the occurrence of two types of serpentinite bodies. The first type is serpentinites associated with the Upper Cretaceous ophiolite complexes in the upper allochthon, while the second type is serpentinite imbricates in the lower allochthon (Fig.1), which mostly occur along thrust-faults, and juxtapose the metamorphosed Cretaceous volcano – sedimentary successions with the underlying metamorphosed Tertiary volcanic – sedimentary succession of Walash – Naopurdan Group (Aswad, 1999 and Jassim *et al*., 2006). For further discussion to the tectonic model; refer to Aziz (2008). Bolton (1958) referred to the association of serpentinite with thrust faults in NE Iraq. Jassim (1973) assumed that serpentinization occurred at various stages, during initial emplacement in the Late Cretaceous and during Late Miocene thrusting. A recent study (Aziz, 2008) concluded that serpentinite occurrences within the Zagros Suture Zone are divided into two groups: **1)** Highly sheared serpentinites, which occupy the lower contact of the ophiolitic massifs (ophiolite – serpentinite association), and **2)** Ophiolitic mélange serpentinites (imbricate) on the base of the lower allochthonous nappe showing block-in-matrix aspect. In this regard, the geochemical fingerprint based on REE patterns exhibits two main groups: group one, shows depleted total REE (0.1 – 1 times MORB) and may represent distinctive boninitic magma of island-arc affinity (fore-arc) related to a suprasubduction zone, while group two is characterized by enrichment in the total REE (10 – 30 times MORB). The latter serpentinites represent a meta-ultramafic mélange with its main unit sandwiched between the parautochthonous Qulqula radiolarite (sedimentary mélange), and the allochthonous Walash volcano – sedimentary series along the Zagros Suture line (Aziz, 2008). These serpentinites acted as a lubricant for the exhumation of subducting sediments and altered oceanic crust.

This study offers further discussion based on new information about the geodynamic evolution of ZSZ in conjunction with the available Rb-Sr and Sm-Nd isotopic results on serpentinites from different areas (Fig.1).

ANALYTICAL PROCEDURES

The Rb-Sr and Sm-Nd isotope analyses were preformed using a Thermo Triton Thermal Ionization Mass Spectrometer in static mode at the isotope geology laboratory of the Swedish Museum of Natural History in Stockholm. About 200 mg of fresh samples were weighed into Teflon capsules together with an appropriate amount of mixed ^{147}Sm – ^{150}Nd tracer solution, and dissolved using concentrated HF + HNO3 acids (10:1 mixture) in steel bombs at 205º C for few days. Those samples with the lowest Nd contents weighted duplicate (i.e., 200 mg for each) in separate teflon capsules and combined after dissolution. After the dissolution and evaporation of the HF+HNO_3 mixture, samples were redissolved in 6N HCl in oven overnight. The sample solutions were purified from iron and strontium and REE (as a group) were separated using the "Tru-Spec." ion exchange method. Subsequently, Sm and Nd were separated from each other using "Ln- Spec." method (Pin and Zaiduegui, 1997).

Sm and Nd were loaded on Re double filaments with a Ta activator. Nd was corrected for Sm interference and normalized to ^{146}Nd/ ^{144}Nd = 0.7219. The Sm and Nd contens were calculated from respective spiked analysis, and the unspiked ^{143}Nd/ ^{144}Nd ratio was calculated from the spiked Nd analysis. Strontium was analysed in unspiked form, with Rb and Sr contents obtained from chemical data. Sr was corrected for Rb interference, and normalized to $^{86}Sr/^{88}Sr = 0.1194$. The analytical results together with results from the La jolla Nd standard and the NBS SRM 987 Sr-standard, as well as the BCR-2 rock standard are presented in Tables (1 and 2).

PETROGRAPHY

Mineralogically, the Zagros Suture Zone massive serpentinites consists of serpentine polymorphs mainly lizardite – chrysotile association, which underwent recrystallization and replacement of lizardite to chrysotile, while sheared serpentinite consists of antigorite – lizardite – chrysotile serpentines. Generally, the Zagros Suture Zone's serpentinites reveal the relict of original minerals such as olivine, pyroxene, and Cr-spinel, as well as the formation of several metamorphic assemblages. These mineralogical assemblages indicate that the original ultramafic protolith hazrburgite, dunite, and to a lesser extent lherzolite. The most common textures preserved are of pseudomorphic (Mesh, Bastite, and hourglass) after olivine and pyroxene, which preserves the pre-serpentinization textures of the ultramafic precursor, as well as non-pseudomorphic (interpenetrating and interlocking) textures.

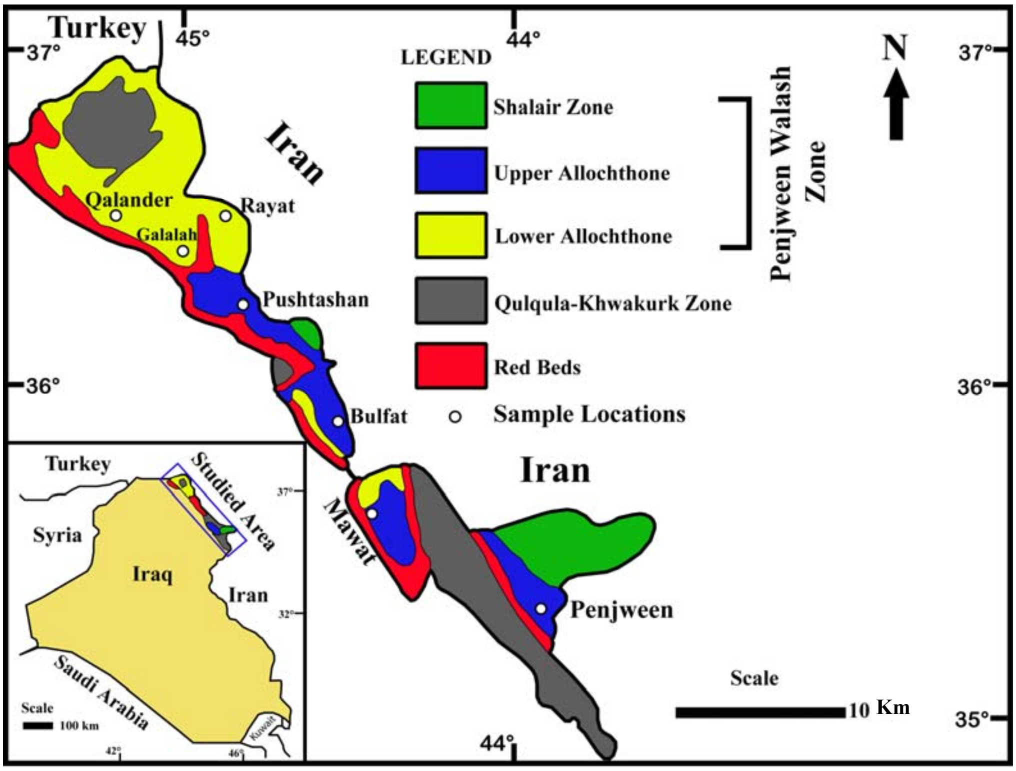

Fig.1: Geological map of the Iraqi Zagros Suture Zone shows the location of the studied areas denoted by open circles, tectonic subdivisions (after Aswad, 1999; and Jassim and Goff, 2006)

ISOTOPIC RESULTS

▪ Rb-Sr

The three collected rock samples from the ophiolite – serpentinite association show limited variation in their initial Sr isotopic composition, calculated at an assumed age of 100 Ma ($^{87}Sr/^{86}Sr_{initial}$ = 0.70392 – 0.70442). This would be close to the mantle value at this time (0.70438; McCulloch and Chappell, 1982). Higher and more variable initial Sr isotope values were noted in the ophiolitic mélange serpentinites ($^{87}Sr/^{86}Sr_{initial}$ = 0.70548 – 0.70677) (Table 1), which may reflect disturbances in their Rb-Sr system. Similarly, the Sr model ages from the ophiolite – serpentinite association display a limited variation (80 – 110 Ma) compared with the huge variation in ages determined from ophiolitic mélange serpentinite rocks (150 – 770 Ma; Table 1). The latter may reflect mixed or disturbed Sr isotope compositions.

Table 1: Rb-Sr isotopic results of ZSZ serpentinite

Sample No.	Rb (ppm)	Sr (ppm)	$^{87}Rb/^{86}Sr$ 1	$^{87}Sr/^{86}Sr \pm 2\sigma_m$ (measured) 2	$^{87}Sr/^{86}Sr(i)$ (100 Ma)	ε_{Sr} (i) 3 (100 Ma)	T_{UR} 3 (Ma)
Ophiolite – serpentinite association (Ophiolite Suite)							
P1A	1.54	1.98	2.25	0.707115 ± 7	0.70392	–6.6	80
M7	0.70	6.02	0.336	0.704844 ± 6	0.70437	–0.2	100
PZ8	0.80	7.28	0.318	0.704874 ± 6	0.70442	+0.6	110
Ophiolitic mélange serpentinites (Imbricate)							
MB	1.05	2.02	1.50	0.707619 ± 7	0.70548	+15.6	150
G10	0.70	1.82	1.11	0.707428 ± 7	0.70585	+20.8	200
HS12	0.50	4.34	0.333	0.707246 ± 9	0.70677	+33. 9	770

1) Rb and Sr contents and $^{87}Rb/^{86}Sr$ ratio from chemical analyses.

2) Sr loaded on single Re filaments with tantalum activator and $^{87}Sr/^{86}Sr$ ratios measured on a Thermo Triton thermal ionization mass spectrometer in static mode, corrected for Rb interference and normalized to $^{86}Sr/^{88}Sr$ = 0.1194. Two runs of the NBS SRM 987 Sr-standard gave $^{87}Sr/^{86}Sr$ ratios of 0.710217 ± 9 and 0.710225 ± 8 ($2\sigma_m$), respectively, and one run of the BCR-2 rock standard gave 0.704975 ± 8 ($2\sigma_m$). Error given as standard deviations of the mean from the mass spectrometer run is in the last digits.

3) εSr-values (calculated at an assumed age of 100 Ma), and T_{UR} Sr model ages according to McCulloch and Chappell (1982): present-day $^{87}Rb/^{86}Sr$ mantle ratio = 0.0827, and present-day $^{87}Sr/^{86}Sr$ mantle ratio = 0.7045.

▪ Sm-Nd

The studied samples show very low Sm and Nd concentrations (0.003 – 0.18 ppm Sm, 0.002 – 0.35 ppm Nd). The measured $^{143}Nd/^{144}Nd$ ratios show variation between 0.512483 – 0.512810 in rocks from ophiolite – serpentinite associates, while rocks from ophiolitic mélange serpentinites show larger variation (0.511101 – 0.513133). On the other hand, εNd values range between (–3.0) – (+3.8) in the former rocks, and between (–30.0) – (+9.7) in the latter (Table 2). Because of that, only two samples, both from the ophiolite suite, gave acceptable analytical results that are reported in Table (2). The Nd model ages (T_{CHUR} and T_{DM}) show scattering compared with Rb-Sr ages.

Table 2: Sm-Nd isotopic results of ZSZ serpentinites

Sample No.	Sm[1] (ppm)	Nd[1] (ppm)	^{147}Sm/ ^{144}Nd1	^{143}Nd/ ^{144}Nd $2\sigma_m$[2]	ENd[3] (present)	εNd[3] (initial)
Ophiolite – serpentinite association (Ophiolite Suite)						
P1A	0.007	0.036	0.1169	0.512483 ± 17	–3.0	–2.0
M7	0.029	0.147	0.1205	0.512810 ± 17	+3.4	+4.3
Basalt standard						
BCR-2	6.65	28..9	0.1391	0.5126245 ± 3	–	–
PZ8	0.013	0.059	0.1372	0.512831 ± 94	+3.8	+4.5
Ophiolitic mélange serpentinites (Imbricate)						
MB	0.004	0.016	0.1635	0.511101 ± 112	–30.0	–29.6
G10	0.003	0.002	0.7281	N.D.	N.D.	N.D.
HS12	0.178	0.352	0.3063	0.513133 ± 66	+9.7	+8.3

1) Sm and Nd contents and ^{147}Sm/ ^{144}Nd ratio from isotope dilution analysis with combined ^{147}Sm – ^{150}Nd tracer.

2) ^{143}Nd/ ^{144}Nd ratios calculated from ID run, corrected for Sm interference and normalized to ^{146}Nd/ ^{144}Nd = 0.7219. Two runs of the La Jolla Nd-standard during the measurement periods gave a ^{143}Nd/ ^{144}Nd ratio of 0.511847 ± 5 ($2\sigma_m$) and 0.511849 ± 2 ($2\sigma_m$), respectively. Error given as 2 standard deviations of the mean from the mass spectrometer run in the last digits, all analyses were carried out at the Thermo Triton mass spectrometer.

3) Present-day and initial ε_{Nd} values (at an assumed age of 100 Ma), according to Jacobsen and Wasserburg (1984): present-day chondritic ^{147}Sm/ ^{144}Nd ratio 0.1967, present-day chondritic ^{143}Nd/ ^{144}Nd ratio 0.512638.

DISCUSSION

To elucidate the controversy related to petrogenesis and timing of formation and emplacement of serpentinites, isotopic composition of ^{87}Sr/ ^{86}Sr and ^{143}Nd/ ^{144}Nd have been measured on various serpentinite rocks from distally separated areas (Fig.2). The Sm-Nd system has certain advantages over the Rb-Sr system in terms of serpentinization process. Since Sm and Nd are REE, i.e. fluid immobile, they are less susceptible to low-grade metamorphism, serpentinization, and hydrothermal alteration compared with fluid-mobile Rb and Sr. Thus, only samples from the ophiolite suite gave acceptable Sr model ages (80 – 110 Ma) that well coincide with previously measured K-Ar ages of (97 – 118) Ma (Aswad and Elias, 1988). The ophiolite mélange serpentinites yield higher and more variable Sr model ages and initial ratios, suggesting crustal contamination or open system behavior during metamorphism.

Only two of the Sm-Nd analyses, both from the ophiolite suite, yielded acceptable results, with initial εNd values (at 100 Ma) of –2.0 and +4.3, respectively. In combination with their initial εSr values of –0.2 and –6.6, an origin from a near-chondritic to slightly depleted mantle would be indicated. The low Sm and Nd contents suggest very little influence from crustal rocks. Also the Sr contents are relatively low (1.8 – 7.3 ppm), as would be expected from ultramafic rocks. On the other hand, with these low concentrations, even minor amounts of crustal contamination may have a dramatic effect on the Nd and Sr isotope compositions, making the results difficult to be interpreted. However, investigation of the Rb-Sr isotope determinations (Table 1) reveals two different age patterns between ophiolite – serpentinite associates (80 – 110 Ma), and ophiolitic mélange serpentinites (150 – 770 Ma.). This age variation between the two different serpentinites was even observed within the same region (e.g Mawat) between samples, M_7 and MB (Table 1). In this regard, the Rb-Sr ages of (80 – 110) Ma, which belong to ophiolite – serpentinite associates represent the areas (Mawat, Penjween ; Pauza and Pushtashan) of ophiolitic massifs of the upper allochthon. This Period (80 – 110 Ma.) is positively correlated with K-Ar ages (97 – 118 Ma) (Albian – Cenomanian) of spilitic diabase from the subvolcanic rocks of Mawat ophiolite complex interpreted as the time of ophiolite formation and/ or hydrothermal ocean-floor metamorphism (Aswad and Elias, 1988 and Farjo, 2006). On the other hand, older ages (150 , 200 , and 770 Ma), obtained from rock samples collected from areas of Qalander, Rayat, Galalah, Halsho, and Hero represent the base of the lower allochthonous sheets (Walash Series) of age dated (32 – 44) Ma (Koyi, 2006). These rock samples were classified as of serpentinitic mélange type. However, the complex mixture of rock types of various compositions (ultramafic, mafic, and sedimentary), which constitute the mélange serpentinites may reflect such type of non-consistent and disparate ages. From this variability in age determination, it is hard to detect a definite absolute age for any specific event. Thus, a significant evidence for such variable and mixed ages is the occurrence of mélange phenomenon. In this context, the sample of 770 Ma age probably represents Neo-Proterozoic Arabian oceanic lithosphere (Jassim, Personal communication), or would rather be related to the Sanadaj – Sirjan Zone activity of Iranian micro-continent.

In order to facilitate interpretation and presentation of Nd isotopic data, the epsilon notation εNd is employed. The studied samples display a clear variation in the Nd isotope composition especially the εNd ranging between (–30.0) – (+9.7) (Table 2). The negative values of εNd obtained from two samples, P1A (ophiolite – serpentinite associate) in which εNd = –3.0, and ratios $^{143}Nd/^{144}Nd_{measured}$, and $^{87}Sr/^{86}Sr_i$ are 0.512483, and 0.70392 respectively. The other sample MB (ophiolitic mélange serpentinite) shows a very low εNd = –30.0, and ratios $^{143}Nd/^{144}Nd_{measured}$, and $^{87}Sr/^{86}Sr$ are 0.511101, 0.70548, respectively. These two samples with negative εNd values represent a crust-derived rocks originated from enriched mantle source (EMI) (Fig.2). The value of εNd = –30.0 (Sample MB) would correspond to a $^{143}Nd/^{144}Nd$ ratio of 0.5111, and could refer to a typical value for Pre-Cambrian metasediments (Jacobsen and Wasserburg, 1979). On the other hand, samples with positive εNd values are mantle-derived rocks (Fig.2), in particular sample HS12 with the highest $^{143}Nd/^{144}Nd_{measured}$ = 0.513133, $^{87}Sr/^{86}Sr$ = 0.70677 ratios, and εNd = +9.7 was generated from Rb-enriched mantle (EMII) (Fig.2). It seems that a value of εNd = +9.7 (Sample HS12) would correspond to a $^{143}Nd/^{144}Nd$ ratio of 0.51313, may refer to a typical value for mid-oceanic ridge basalt (Jacobsen and Wasserburg, 1980). The latter can be interpreted to have been derived from the mantle source that was affected by severe crust-mantle interaction. The dispersion characteristic of isotope composition of serpentinites, especially those of ophiolitic mélange (imbricate) type is indicative of contamination reflecting either, an enrichment of the mantle wedge by fluids derived from subducted meta-sediments, and/ or a latter contamination by continental country rocks during the emplacement process. The present age data with the absence of metamorphic sole, suggests that the time of final emplacement of serpentinites (associated with ophiolite massifs) on top of Walash volcano-sedimentary sequence aged (32 – 43 Ma) (Koyi, 2006), probably occurred post 30 Ma. In terms of ophiolitic mélange serpentinites, it seems that this type was emplaced on top of Red Beds clastic Series post Paleocene – Eocene, as this serpentinites feed the Upper member of Tanjero Formation (Late Maastrichtian), and Tertiary molasse basin (uppermost Paleocene – Eocene).

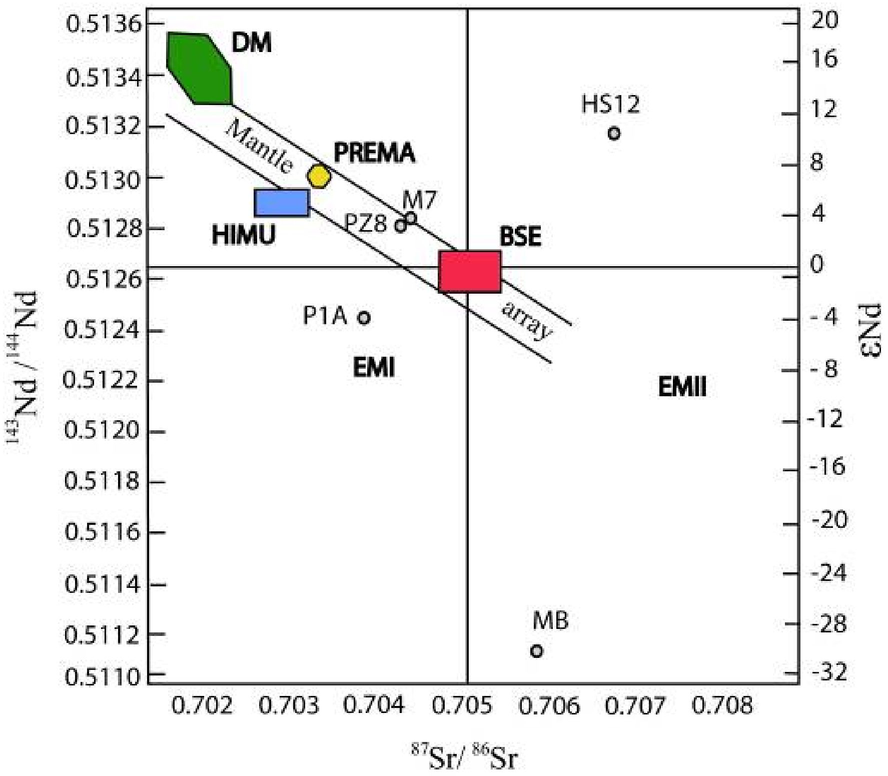

Fig.2: Broader isotopic context of the Zagros Suture Zone serpentinites (DM depleted MORB mantle, EMI enrich mantle I, EMII enrich mantle II, BSE bulk silicate Earth, HIMU high μ mantle,□□ and□□ PREMA prevalent mantle)

CONCLUDING REMARKS

The most significant remarks that can be drawn from the available Sr-Nd isotopic data of serpentinites from various areas along the line of Zagros Suture Zone are:

1) The Rb-Sr age data yield two distinct episodes of (80 – 110) Ma (ophiolite – serpentinite associates), and (150 – 770) Ma (ophiolitic mélange serpentinites).
2) The younger episode of (80 – 110) Ma obtained from serpentinites represent the base of ophiolite complexes (e.g. Mawat, Penjween, and Bulfat) is strongly correlated with the previous published K-Ar ages of hornblende (97 – 118 Ma) from the volcanic part of Mawat-ophiolite complex. Therefore, this period (Albian – Cenomanian) represents the age of ophiolite formation as well as the subsequent hydrothermal ocean-floor metamorphism, and/ or serpentinization, as the time span is so limited between ophiolite formation and accompanied metamorphism, and both processes were associated with the occurrence of suprasubduction zone (SSZ).
3) The orogenic igneous activity responsible for the genesis of ophiolite – serpentinite associates was influenced by the first older intraoceanic suprasubduction Zone (~ Albian – Cenomanian) of island-arc affinity (fore-arc) at the Palaeo-ridge or proximal to it. Because of the absence of metamorphic sole, the approximate age of emplacement of these serpentinites was ~ 30 Ma., i.e., posts dating the volcanicity of Walash sequence (32 – 43 Ma).
4) The older episode (150 – 770 Ma) determined from ophiolitic mélange serpentinites (imbricate) demonstrates the pronounced heterogeneity and clear regional variation in the isotopic composition of various hybridized rock types due to the effect of mélange phenomenon. This mixed age implies the difficulty of detecting a definite absolute age.

5) The tectonic activity affecting the generation of ophiolitic mélange serpentinites is the second younger intra-oceanic suprasubduction zone (~ Late Maastrichtian) of Walash volcano – sedimentary sequence of island-arc and calc-alkaline affinities (fore-arc). These serpentinites were probably emplaced post Paleocene – Eocene.
6) The isotopic composition of strontium ($^{87}Sr/^{86}Sr_i$ = 0.70392 – 0.70677) and εNd = (–30.0) – (+9.7), suggests that the parent magma was originated from enriched-upper mantle source, particularly those serpentinites from ophiolitic imbricates, resulted from, either an influx of fluids from a subducted continental slab, which with time; would develop isotopic heterogeneity, and/ or a later contamination from a continental country rocks during the emplacement process.

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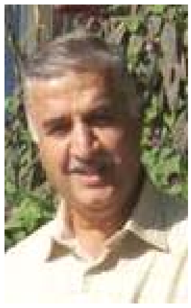

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