Strontium Isotope Ratios as a Tool for the Origin of Barite Mineralization of Marsis and Lefan Deposits/ Northeast Zakho / Iraq

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ABSTRACT

Veins, vienlets, pockets and cavity- filling deposits of barite are found to be associated with Upper Jurassic Formations (Marsis deposit) and Upper Cretaceous Bekhme Formation (Lefan deposit). The strontium isotope ratios of barite are presented here and the data are used to understand the source and origin of barite. The relation of barite mineralization with carbonate host rocks reveals a stratabound epigenetic origin. The obtained $^{87}Sr/^{86}Sr$ ratios range from 0.708226 to 0.708452; these values reveal the possibility of involvement of crustal Sr in the deposition of Marsis and Lefan barite. Isotopic data reveal that strontium in barite was derived from coeval seawater of Late Cretaceous and other processes like mixing of low temperature hydrothermal solution derived from the crust that was rich in radiogenic ^{87}Sr.

نسب نظائر السترونتيوم كاداة لمعرفة أصل تمعدنات البارايت لترسبات مارسيس و ليفان / شمال شرق زاخو/ العراق

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الملخص

تتواجد ترسبات البارايت على شكل عروق وعريقات وجيوب مائلة للفراغات مترافقة لتكاوين الجوراسي الأعلى (ترسبات مارسين) ولتكوين بخمة ذات العمر الكريتاسي الأعلى (ترسبات ليفان).تم دراسة نسب نظائر السترونتيوم لاستخدامها في فهم مصدر واصل ترسبات البارايت في منطقتي الدراسة.

إن علاقة تمعدنات البارايت مع الصخور الكاربوناتية المضيفة تستدل على كون البارايت من نوع المرتبط طباقيا (stratabound) و لاحقة المنشا (epigenetic). تراوحت نسب $^{87}Sr/^{86}Sr$ بين 0.708226 و 0.708452 و تدل هذه القيم على احتمال مشاركة القشرة الأرضية في تكوين ترسبات البارايت لمنطقتي مارسين و ليفان. تشير معلومات النظائر أن السترونتيوم في البارايت مشتق من مياه البحر للعصر الكريتاسي المتأخر بالاشتراك مع محاليل واطئة الحرارة مشتقة من القشرة الأرضية الغنية بالسترونتيوم المشع ^{87}Sr.

INTRODUCTION

It is well understood that strontium isotope geochemistry of barite provides an insight to the source and the origin of this mineral (Sharma *et al.*, 2003; Fei *et al.*, 2004; Ayuso *et al.*, 2004).

Strontium can enter the lattice of mineral structures such as calcite, fluorite, gypsum, and barite. it is similar to Ba and Ca in geochemical characteristics. Strontium isotope composition of these minerals, when formed in equilibrium with seawater directly records the strontium isotope composition of the coeval seawater. The main assumptions for the use of $^{87}Sr/^{86}Sr$ ratio as tracer of various geological processes is that at any given time the oceans contain well mixed Sr isotopes and that strontium isotope ratio of oceans changed during geological evolution. These changes have been induced by variations in the relative inputs of Sr to the oceans after decay of Rb (Barbieri *et al.*, 1998).

From meteorite analysis (where Rb is almost absent), the earth's primordial Sr have an initial $^{87}Sr/^{86}Sr$ ratio of 0.699 at the birth of the earth (4.5 B.Y. ago). The mantle contains a small amount of Rb, and as a result its $^{87}Sr/^{86}Sr$ ratio has grown from 0.699 to about 0.7037 over the course of geological time. The average $^{87}Sr/^{86}Sr$ of the earth crust has been growing through geological time due to the enrichment of Rb content, reaching an average value of about 0.719 at the present day. On the other hand, sedimentary rocks have much higher $^{87}Sr/^{86}Sr$ ratios because of the huge amount of rubidium Rb in the earth is concentrated in the crust (Hall, 1987).

GEOLOGICAL SETTING

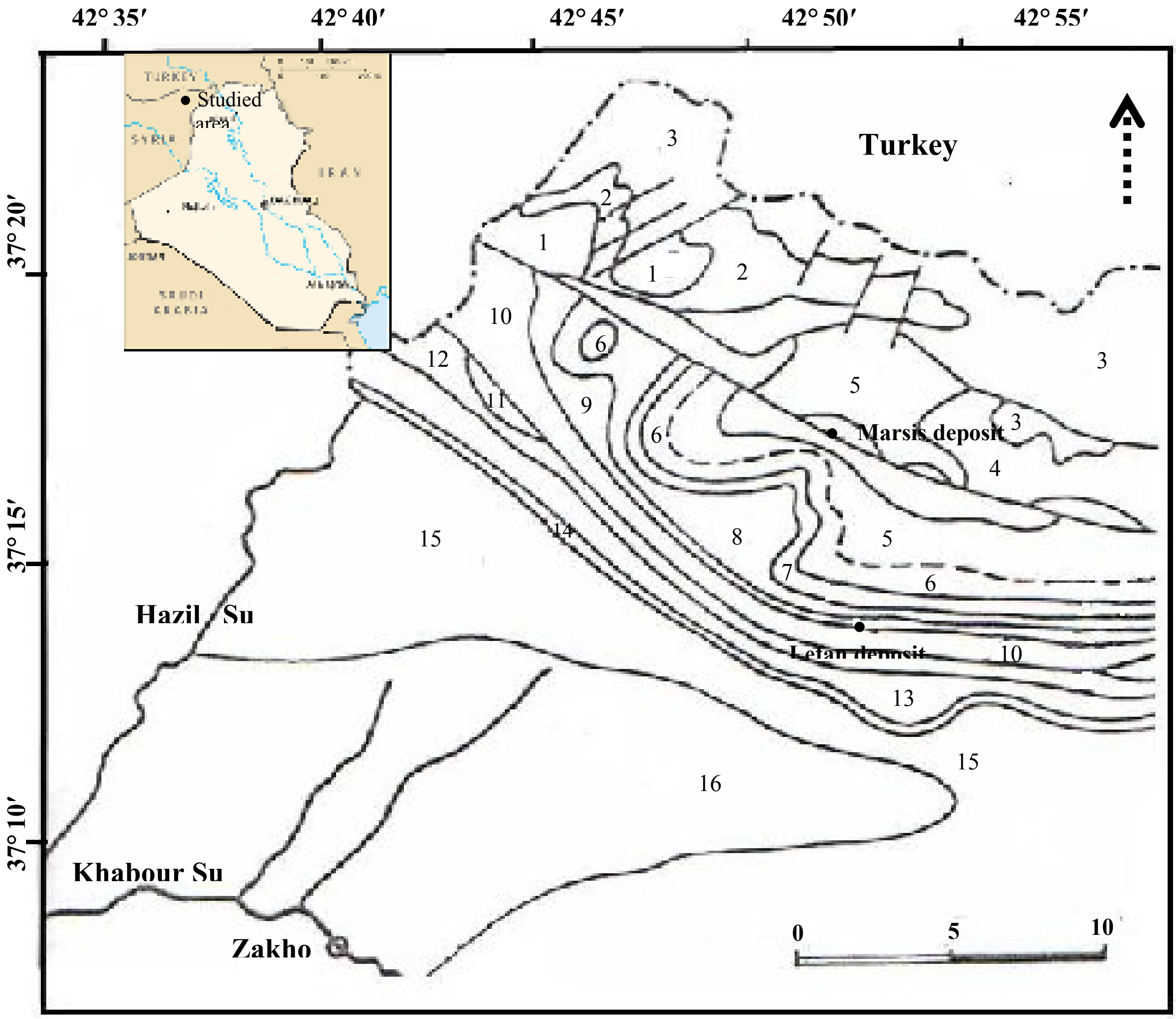
Two areas containing barite deposits are studied. These are Marsis and Lefan located Northeast of Zakho city, within the Northern Thrust Zone, North of Iraq (Fig.1). These deposits are hosted within carbonate rocks. The field observations show that the mineral deposits in Marsis are hosted in Units B and C of Upper Jurassic rocks (Al-Ka'aby and Al-Azawi, 1992). While they embedded within Bekhme Formation (Upper Cretaceous) partially extending into Shiranish Formation age (in Lefan area) (Al-Ka'aby and Al-Azawi, 1992; Awadh, 2006).

Marsis area is about 25 km to the Northeast of Zakho city. The area is highly mountainous and characterized by the presence of cliffs and steep slopes. The area is crossed by three main valleys that intersect to form Basa Agha valley which flows to the west.

The stratigraphic section in Marsis area consists mainly of carbonate rocks of about 590m thick representing geological time from Upper Jurassic to Upper Cretaceous. There is a large variation in the thickness due to tectonic activities during deposition (Ma'ala *et al.*, 1990).

The Jurassic sediments about 63m thick crop out in the northern block of a major reverse fault (Fig. 1). The distinction between the Upper Jurassic sediments in this area is very difficult due to dolomitization of most fossils. Therefore, Al-Ka'aby and Al-Azawi (1992) subdivided these rocks into three units according to field observations (Fig. 2). Unit A is the older unit composed of dolomitic rocks, gray to dark gray in color, fine crystalline, very hard and highly resistant to the erosion that forms a cliff and nearly vertical slopes. Unit B is olive green, recrystallized and brecciated dolomitic limestone And characterized by the presence of vienlets and pockets of barite with some voids. Unit C includes dark gray to black dolomitic limestone, coarse grained, sandy texture, with voids, easily disaggregates, and forms gentle slopes. Predominantly, the fractures and voids are filled with barite.

Lefan location is about 5 km to the south of Marsis location (Fig. 1). The mineralization is located within Bekhme Formation and partially extends into Shiranish Formation. Bekhme Formation is composed of bituminous secondary dolomite, replacing organic detrital limestone in its upper part, and reefal detrital limestone in the middle part, with basal breccia conglomerate in the lower part (Jassim and Goff, 2006). Shiranish Formation conformably overlies the Bekhme Formation, composed of thin bedded argillaceous limestones (locally dolomitic) overlain by blue pelagic marls (Bellen *et al.*, 1959; Jassim and Goff, 2006).



١٦	U. Bakhtiari (Pliocene- Pliestocene)	٨	Qamchuqa (M. Cretaceous)
١٥	U. Faris (U. Miocene)	٧	Sarmord Formation (L. Cretaceous)
١٤	Anah Formation (Oligocene)	٦	M.& U. Jurassic Formations
١٣	Pila Spi (M.- U. Eocene)	٥	Sehkaniyan and Sarki Formations (L. Jurassic)
١٢	Gercus Formation (L. Eocene)	٤	Kurra Chine Formations (U.Triassic)
١١	Kolosh Formation (Pliocene)	٣	Serwan Formation (Triassic)
١٠	Shiranish Formation (U. Cretaceous)	٢	Chia Zairi Formation (U.Permian)
٩	Aqra/Bekhme (U. Cretaceous)	١	Ora Formation (L. Carboniferous)

Fig. 1: Location and geological map of NE Zakho, (McCarthy and Smith, 1954).

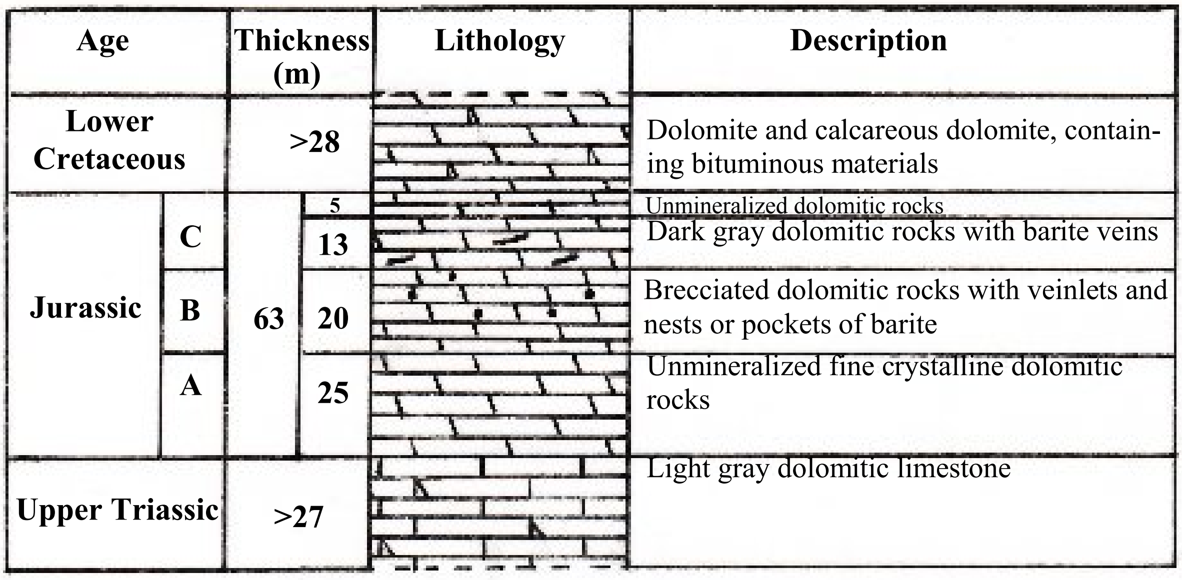


Fig.2: Typical columnar section for barite deposits in Marsis location/ Zakho (Al-Ka'aby and Al-Azawi, 1992).

SAMPLING AND ANALYTICAL METHOD

Four samples of barite which were collected from veins in Marsis (2 samples) and cavities filling in Lefan (2 samples) deposits, analyzed for $^{87}Sr/^{86}Sr$ ratios and the results are presented in Table 1.

Table 1: Strontium Isotope Ratios of Marsis and Lefan Barite Deposits.

Locality	**Sample**	**$^{87}Sr/^{86}Sr$**	**1δ**
Marsis	M1	0.708246	±0.000004
Marsis	M2	0.708272	±0.000007
Lefan	L1	0.708226	±0.000004
Lefan	L2	0.708452	±0.000004

The Sr isotope composition was analyzed in Swedish Museum of Natural History/ Laboratory for Isotope Geology. Sr isotope ratio was measured on a Thermo Scientific TRITON Thermal Ionization Mass Spectrometer (TIMS). Measured ^{87}Sr intensities were corrected for Rb interference using $^{87}Rb/^{85}Rb$= 0.38600 and ratios were reduced using the exponential fractionation law and $^{88}Sr/^{86}Sr$= 8.375209. The external precision for $^{87}Sr/^{86}Sr$ as judged from running NBS987 standard is 16ppm (n=33). No accuracy correction had to be made, while the $^{87}Sr/^{86}Sr$ ratio for the measure standard was $0.710221\pm1x10^{-6}$, which is the same to the theoretical value of the standard.

RESULTS AND DISCSSION

The barite deposits are restricted to a fairly limited stratigraphical range within the Late Jurassic rocks of units B and C (Marsis deposit) and of Late Cretaceous age (Lefan deposit); therefore, they are considered as strata-bound deposits

(Al-Ka'aby and Al-Azawi, 1992; Awadh, 2006). The analytical results of the analyzed four samples are listed in (Table 1).

Wang and Chu (1993) reported a group of Sr isotope data ranging from 0.708027 to 0.708810 based on the measurement of barite samples of Late Sinian to Early Cambrian in south China, which are lower than that of coeval seawater and marine carbonate, and as a consequence, they proposed that the sedimentation of the barite was closely related to submarine volcanic or hydrothermal activities.

The $^{87}Sr/^{86}Sr$ ratios in this work range between 0.708226 and 0.708452, which are very close to each other and similar to those reported by Wang and Chu (1993). The ratios are higher than those of coeval seawater in marine carbonate of Late Cretaceous- Oligocene between 0.7073- 0.7078 (Figs 3 and 4).

Fluid inclusion study carried out on one sample of Lefan barite deposit suggested that it occurred in an aqueous solution with salinity of 15.5 wt% NaCl equiv. and formed at very low temperature ranging between 50°C to 60°C (Awadh, 2006).

The absence of any large scale Pb- Zn- fluorite mineralization in association with barite may rule out the possibility of its high temperature hydrothermal origin (Sharma *et al.*, 2003). The presence of rose like shape in the barite deposits is another indication for the deposition at a low temperature (Ayhan, 2001; Paytan *et al.*, 2002; Paradis *et al.*, 2004).

Strontium isotope composition of seawater is mainly controlled by Sr from the crust and mantle (basalt). Strontium from the crust is principally provided by weathering of the ancient continental rocks, its $^{87}Sr/^{86}Sr$ ratio is comparatively high (average value 0.7119), because the materials from the crust are rich in Rb (Palmer and Edmond, 1989). While Sr from the mantle is mostly derived from mid-ocean ridge hydrothermal system, where $^{87}Sr/^{86}Sr$ ratio is comparatively low (average value 0.7035), due to the depleted of material from the mantle Rb (Palmer and Elderfield, 1985). The present- day average value of global seawater $^{87}Sr/^{86}Sr$ ratio is 0.70973 (Denison *et al.*, 1994) as shown in Figure 4. Sr isotope composition and evolution of seawater are effected by such global events as the change of mid- ocean ridge hydrothermal system, the change of the global sea level and the global catastrophic events and so forth (Jones *et al.*, 1994; Fei *et al.*, 2004; Huang *et al.*, 2004).

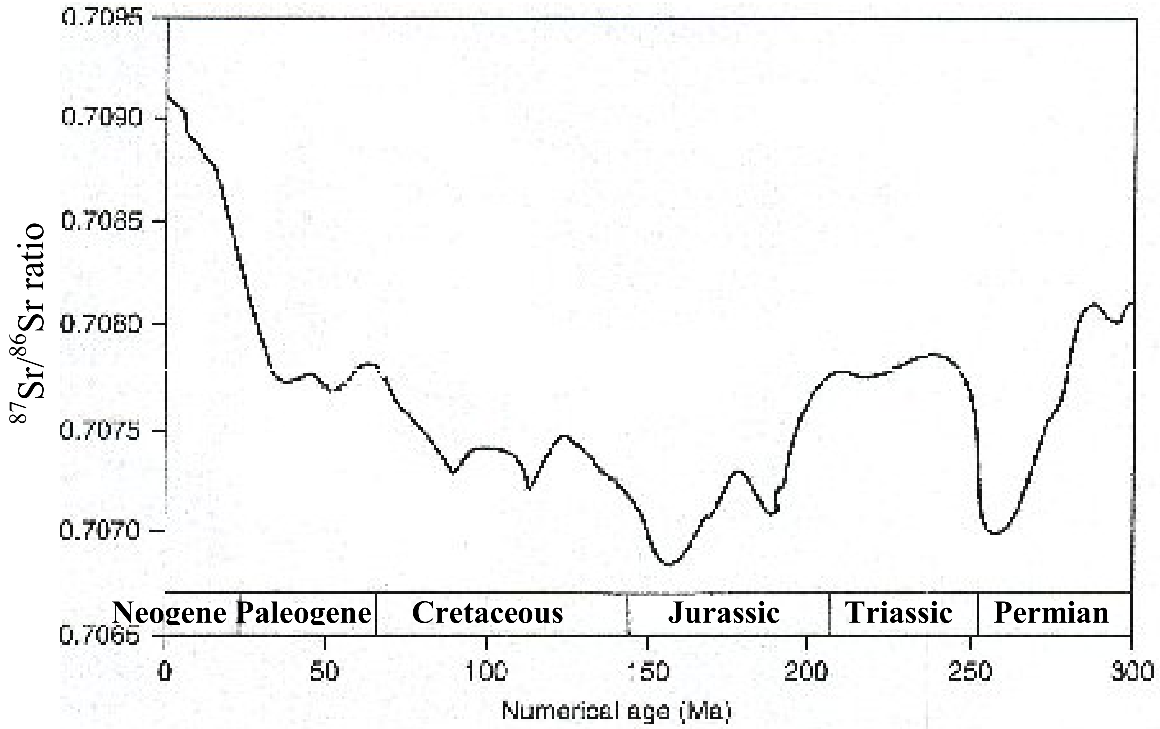


Fig. 3: Seawater Strontium Isotope Curve from Permian to Neogene (McArthur *et al.*, 2001).

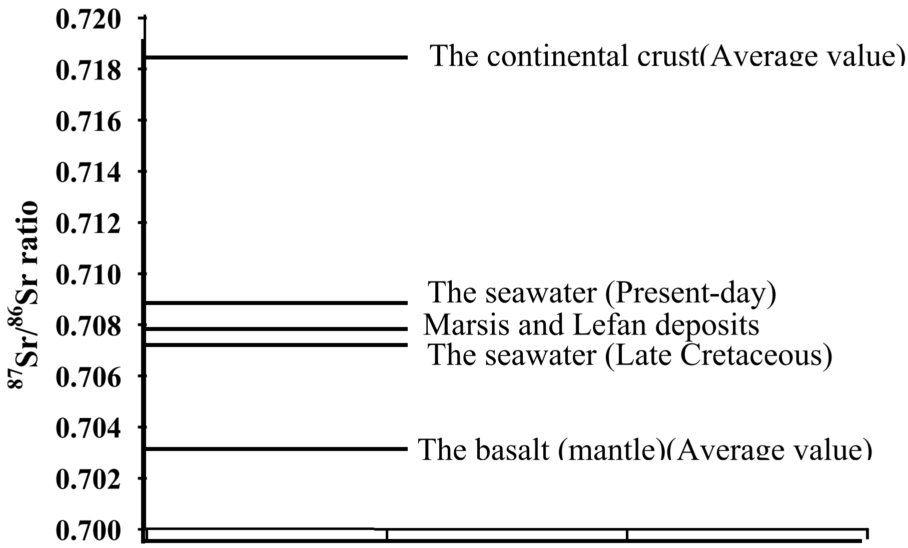


Fig.. 4: The Correlative Chart of Sr Isotope Composition of Different Barite Deposits, Rocks and Seawater (Modified from Fei *et al.*, 2004).

Therefore, Sr isotope composition and evolution of marine carbonate and sulphate, which did not experience diagenetic alteration, could reflect the composition of the coeval seawater and are important geochemical proxies for the global events. To certain extent, the Sr isotope composition of global seawater is homogeneous because the residence time of Sr in seawater (about 10^6a) is longer than that of global seawater circulation (Denison *et al.*, 1994).

Fei *et al.* (2004) reported $^{87}Sr/^{86}Sr$ ratios of the layered barite deposits, from east Guizhou (China), between 0.708310 and 0.708976 which are lower than those of coeval marine carbonate of Early Cambrian (0.7090), showing that Sr with low $^{87}Sr/^{86}Sr$ ratios was from seafloor volcanic or hydrothermal activities. Suggesting that the Sr in barite is not all from seawater and partially might be from the mantle which have low $^{87}Sr/^{86}Sr$ ratio. While the two other samples from barite vein and nodule (east Guizhou) have higher $^{87}S/^{86}Sr$ ratios (0.709585 and 0.709537) than coeval marine carbonate, possibly is due to involvement of radiogenic terrigeneous source in sediments (Jones *et al.*, 1994; Paytan *et al.*, 2002).

From Late Cretaceous to Oligocene, the seawater $^{87}Sr/^{86}Sr$ ratio had been globally elevated than the Late Jurassic, and reached to 0.7078 by the Late Cretaceous (McArthur *et al.*, 2001). Marsis and Lefan barite deposits were formed in Late Cretaceous. Awadh (2006) studied the sulfur isotopes of galena that associated with barite in Lefan area, and he concludes the age between Late Cretaceous and Oligocene. The barite $^{87}Sr/^{86}Sr$ ratios of these two deposits between 0.708226 and 0.708452 are higher than those of coeval seawater (Fig. 4). Suggesting that the Sr in barite is not all from seawater and partially might be from the terrigeneous source through water-rock interaction, and as a consequence, it is proposed that the Late Cretaceous barite deposits should be a product of the low temperature hydrothermal fluids. These fluids are ascending upward through the faults and fractures that may be related to episodic deformation of the rocks during Laramide Orogeny in the Late Cretaceous (Awadh, 2006).

CONCLUSIONS

The barite $^{87}Sr/^{86}Sr$ ratios of Marsis and Lefan deposits, between 0.708226 and 0.708452, are similar to each other, which might have the same source and origin. These ratios are greater than those of coeval marine seawater of Late Cretaceous to Oligocene (0.7073- 0.7078), showing that the Sr in barite is not all from seawater but is partially from involvement of terrigeneous source sediments that interacts with the low temperature hydrothermal solutions that formed this deposits. The suggested age of these mineralization is Late Cretaceous or younger.

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