# Sulphur isotopic study on barite mineralization of the Tons valley, Lesser Himalaya, India: Implication for source and formation process

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**Sulphur isotopic study on barite ($BaSO_4$) mineralization, located about 65 km NW of Dehra Dun in the Tons valley, Lesser Himalaya, has shown that $d^{34}$S values of barite vary from +26.5 to +29.5‰. The data, coupled with earlier published abnormally high value of $^{87}$Sr/$^{86}$Sr in barite (0.720448 to 0.728637), have demonstrated that sulphur was derived from Proterozoic sea water and Ba was obtained from the radiogenic crustal source. These isotopic signatures suggest mixing of sea water sulphate with Ba-carrying crustal fluid for barite formation, with its initial deposition linked to diagenesis of the host rocks.**

**Keywords:** Barite, fluid mixing, Lesser Himalaya, sulphur isotope.

BARITE in the Lesser Himalaya shows affiliation with siliciclastic and calcareous host rocks. It occurs at the Andhra Kumla village, Sirmur district and is extended to the Kherwa area in the Tons valley, NW of Dehra Dun. Here, purple-grey coloured siliciclastic rocks of the Nagthat formation host white, crystalline and off-white massive-type barite[1,2]. We present here S-isotopic study of barite, and the data, together with the published $^{87}$Sr/$^{86}$Sr values, are used to probe the source of S and Ba as well as the process during its formation.

The Lesser Himalaya, bounded in the south by the Main Boundary Thrust and in the north by the Main Central Thrust, comprises Proterozoic to Cambrian marine sedimentary formations with nappes of crystalline rocks. Sedimentary sequences of this geotectonic zone include the Berinag, Damta, Deoban and Krol Groups, whereas the main crystalline units are Ramgarh and Almora nappes, Lansdowne, Banali, Satengal, Askot, Baijnath and Jutogh klippe[3]. A brief outline of the geology of the area (77°45′–77°48′: 30°33′–30°56′, Figure 1 *b*) is given in Table 1. For a detailed regional geological set up of the Lesser Himalaya, the reader is referred to Valdiya[3].

The study area is occupied by rocks of the Chandpur, Nagthat, Blaini and Krol formations of Lesser Himalaya (Figure 1). Major portion of the study area is covered by metamorphosed flysch of the Chandpur Formation consisting of olive-grey-coloured slates and phyllites intercalated with siltstones and greywacke. They are overlain by purple–grey, white-coloured massive and laminated, hard siliciclastic rocks of the Neoproterozoic Nagthat Formation, which is an integral part of Krol belt succession. These siliciclastics are deposited in a shallow tidal sea representing continental shelf deposition of sand bar-shore complex environment[4,5]. Petrographic studies, palaeocurrent direction and geochemical evidences suggest that material for the formation of Nagthat siliciclastics hosting barite mineralization was derived from Archaean Banded Gneissic Complex[5,6]. Nagthat Formation is overlain by Blaini formation consisting of conglomerates, slates, sandstones and localized limestones.

Barite occurs as lenses, veins, pockets and pods in the siliciclastic rocks of Nagthat Formation. Pockets of barite in siliciclastic rocks and vice-versa are seen in the mineralized zone. At times, veins of barite show co-folding with the host rocks (Figure 2 *a*). Under the microscope, barite is euhedral to subhedral with perfect three-set rhombic cleavage and varies in size between 0.01 and 1.0 mm. The XRD pattern shows that it is monomineralic without any celestite. It is bimodal as primary (original) coarse grains and fine recrystallized grains (Figure 2 *b*) occur together. Recrystallized barite granulating along the fractures

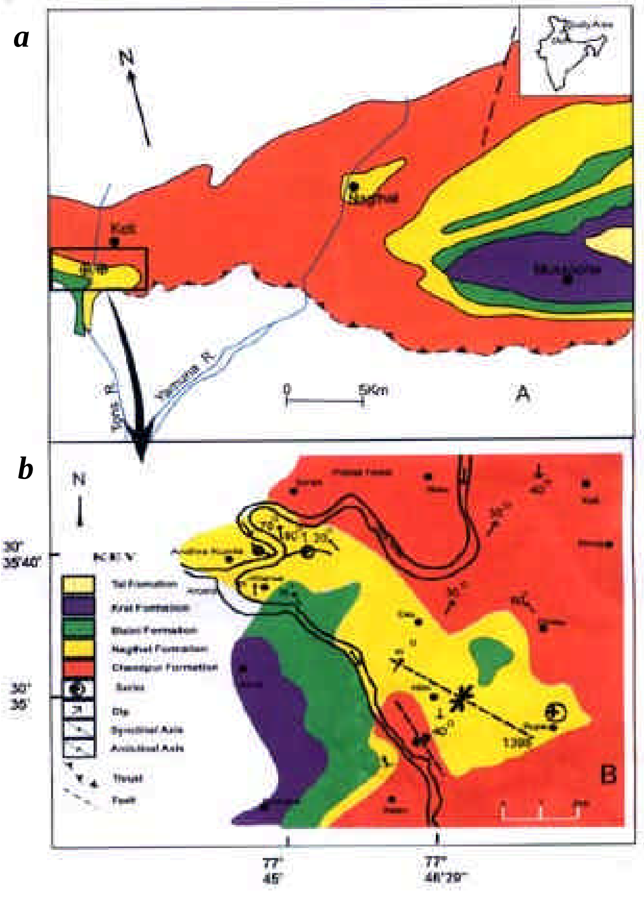

**Figure 1.** ***a***, Regional geological map of part of Mussoorie syncline (after Valdiya[3]). ***b***, Geological map of the area around studied barite mineralization (modified after Auden[20]).

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**Table 1.** Geological succession of Lesser Himalaya around the study area

| Age | Formation | Lithology |
|---|---|---|
| Proterozoic | Krol Formation | Dolomitic limestone, dolomite, calc-argillites, lenses of gypsum, conglomerate |
| | Infra Krol Formation | Shale, siltstone, argillaceous limestone and thin layers of siliciclastic rocks |
| | Blaini Formation | Boulder bed, slate, conglomerate, grey siltstone, argillite, minor quartzite |
| | Nagthat Formation | Siliciclastic rocks and subordinate argillites, phyllite |
| | Chandpur Formation | Grey–green–maroon phyllite, slate and shale |
| | Mandhali Formation | Phyllites, slates, interbedded limestone and boulder bed |

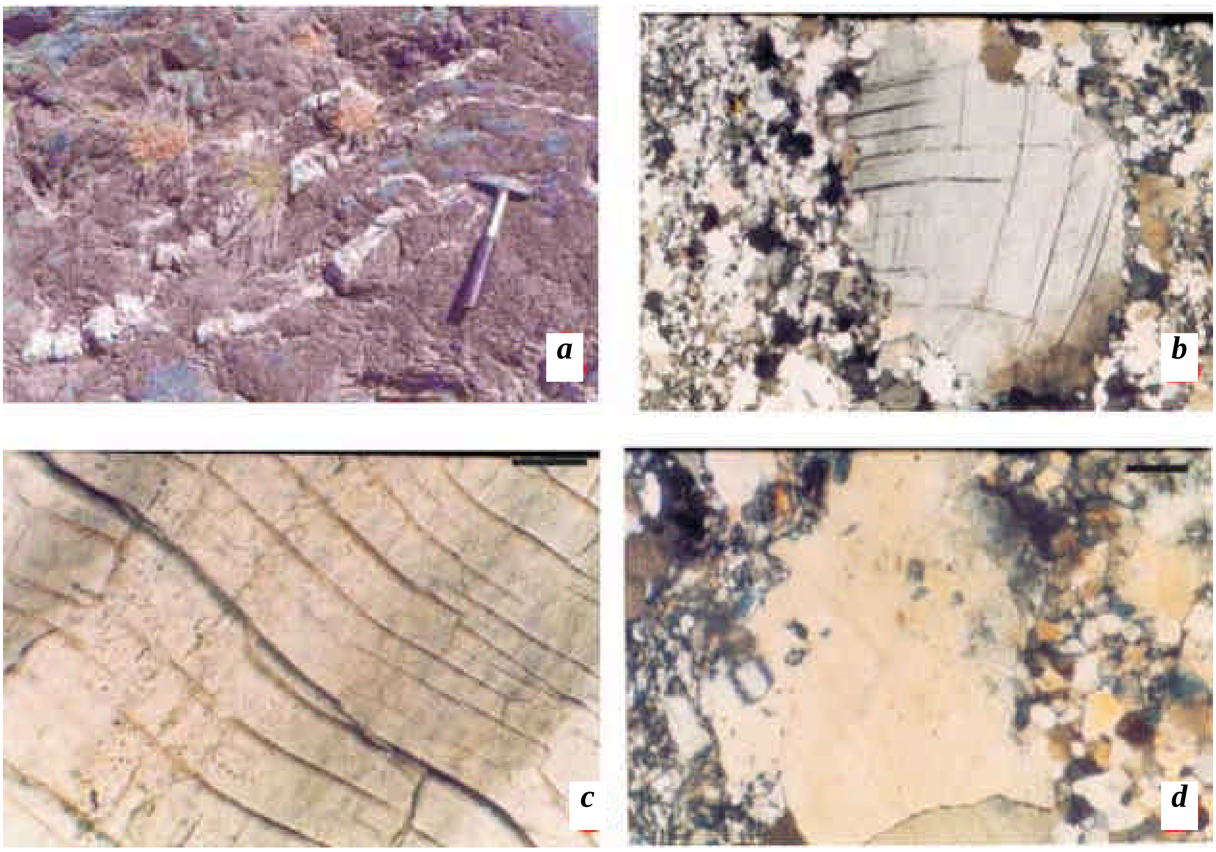

**Figure 2.** ***a***, Photograph showing barite veins co-folded with host Nagthat siliciclastics near Kumla-Andhra in the Tons valley. ***b***, Photomicrograph of bimodal grain fabric in barite. Bar scale = 0.02 mm. ***c***, Photomicrograph of bending of cleavage planes in barite. Bar scale = 0.01 mm. ***d***, Bimodal grains in host siliciclastics. Bar scale = 0.2 mm.

and margins of coarse barite grains, led to mortar texture. Coarse barite grains exhibit sutured boundaries, deformational lamellae and bending of cleavage (Figure 2 *c*). Recrystallized barite grains show annealing texture with perfect triple-point junctions. Under the microscope, host siliciclastic rocks illustrate locomorphic to phyllomorphic stages of diagenesis. Round detrital quartz grains with overgrowth of silica and mica minerals (Figure 2 *d*), represent locomorphic stage, whereas development of schistosity during late diagenesis characterizes phyllomorphic stage. These siliciclastics consist of detrital monocrystalline and polycrystalline quartz, constituting >80% of the sand-size fraction. Like barite, it also shows bimodal distribution of coarse and fine sub-angular grains. They are oriented along foliation and, at times, pressure shadows develop with an envelope of muscovite and sericite. In the sub-grain boundaries of quartz, effect of marginal dissolution by mica and clay overgrowth is seen. Feldspar contributes 3 to 7% of the detrital framework component. In addition, rock fragments of chert, phyllite, gneiss, etc., contribute to this detrital framework.

Fresh white barite samples without any contamination and impurities, were selected from 600 MRL level of the Kumla-Andhra mine, the Tons valley for sulphur isotope analysis. The anlaysis was carried out on Carlo Urba combustion device, coupled to a Finnigan continuous flow mass spectrometer at the Laboratory of Isotope Geochemistry, University of Arizona, USA. Sulphate was converted to

$SO_2$; it was separated from $CO_2$ by gas chromatography and from $H_2O$ in an Mg perchlorate trap. Data are reported as $d^{34}$S‰ (parts per thousand) with respect to the Canon Diablo Troilite ($d^{34}$ $S_{CDT}$‰), the international sulphur isotope standard.

Sulphur is widely distributed in nearly all types of natural environments, viz. igneous, metamorphic and sedimentary rocks, organic substances, marine sediments and the oceanic water. It is one of the abundant elements in sea water, forming significant sulphate in the system. A general higher isotopic value for sulphur in sea water is because of heavier isotope partitioning for residual sulphate present therein, whereas lighter isotope of sulphur is fractioned into sulphides. $d^{34}$S is low (0 ± 3‰) in primary magmatic sulphur in oceanic/submarine basalt[7]. The widest range of $d^{34}$ S from –50 to +100‰ is found in sedimentary rocks. In the sediments of continental margins, platform areas and geosynclines, it is in the range of –12.5 to –17‰. In spite of a few exceptions like Kupersciefer, Germany (–5‰) and Eureka mine, New Mexico (–22 to –23‰)[8], values of $d^{34}$S are generally positive for sulphate of sea water/evaporate origin, as observed in many studies, including Leon Mexico (+12 to +17‰)[9], Seirra Del Guadarrma (+15‰)[10], Aravalli (+17 to +21‰)[11] and Aberfeldy (+40‰)[12]. Bacterial reduction also increases the ratio of heavy sulphur in sulphate of sea water, such as that of Japan Sea, and the sea at Peru margin shows a higher $d^{34}$S value of about +84‰, advocating biogenic origin[13].

Barite of the Tons valley (present study) shows enrichment of isotopically heavy sulphur, with $d^{34}$S varying from +26.4 to +29.5‰ (Table 2). This narrow range of data indicates that the barite-forming system was dominated by sulphate from a homogeneous source. This data rules out the possibility of involvement of any magmatic or sedimentary source for the sulphate, as well as sulphate derived from rivers or from isotope fractionation during mineral precipitate. Rather the data of $d^{34}$S: +26.4 to +29.5‰ for the barite under study are well within the range of +23 to +30‰, suggested for the Proterozoic sea water. Claypool *et al.*[14] demonstrated that $d^{34}$S values for marine sulphate of different ages show variation with $d^{34}$S values of sea water of about +30‰ during the Cambrian, probably reduced to +10‰ in the Permian. Later on, it increased irregularly during the Mesozoic and reached its present value of 20‰. Thus, substantial age information for the sulphate of marine origin can be obtained by S isotope geochemistry. Considering the age curve of $d^{34}$S given by Claypool *et al.*[14] and Schidlowski[15], the Tons valley barite appears to be older than 500 Ma. Consequently, $d^{34}$S values in the Tons valley barite strongly favour involvement of Proterozoic sea water for the deposition of barite.

**Table 2.** $d^{34}$S and $^{87}$Sr/$^{86}$Sr values of barite from the Tons valley, Lesser Himalaya

| Locality | Sample | $^{87}$Sr/$^{86}$Sr* | 1*d* | $d^{34}$S |
|---|---|---|---|---|
| Kumla mine | HS 1 | 0.726613 | ± 0.000058 | +26.4 |
| Kumla mine | HS 2 | 0.728637 | ± 0.000039 | +27.7 |
| Kumla mine | HS 3 | 0.720448 | ± 0.000034 | +29.5 |
| Tons river | HS 4 | 0.720705 | ± 0.000039 | NA |

*Data from Sharma *et al.*[16]; NA, Not analysed.

Strontium isotopes are potential to understand the source of barium for barite, and the suggested sources include magmatic, hydrothermal or crustal-derived[11,17]. $^{87}$Sr/$^{86}$Sr ratio in barite is measured as initial strontium ratio because Ba and Sr are part of solid solution series between $BaSO_4$ and $SrSO_4$, and Rb cannot enter into the lattice of barite. Mantle-derived material is characterized by low $^{87}$Sr/$^{86}$Sr ratio (cf. 0.704 ± 0.002), whereas this ratio is high (>0.710) in the continental crustal material. $^{87}$Sr/$^{86}$Sr ratios of various source materials like oceanic floor, ocean islands, sea water and hydrothermal origin have been defined. The strontium isotope ratio of the Tons valley barite (Table 2)[16] varies from 0.720448 ± 0.000034 to 0.728637 ± 0.000039. High $^{87}$Sr/$^{86}$Sr values of 0.7234 ± 0.0003 have also been reported for Aravalli barite[11]. Considering the value of strontium isotope ratio in various processes of barite formation, a highly radiogenic continental source of barium has been suggested for the barite under study[16].

The elevated $^{87}$Sr/$^{86}$Sr ratio of the Tons valley barite can be discussed together with its $d^{34}$S values. Collectively, they are found significant in defining the source of the material and processes involved in barite formation[18]. S and Sr-isotopic data of barite under study are shown on the binary plot (Figure 3). $d^{34}$S isotope values from 26.5 to 29.5‰ attribute that late Proterozoic sea water had participated in the barite formation. This inference is corroborated by the late Proterozoic Nagthat siliciclastic host rocks of shallow marine origin[5], with which barite closely

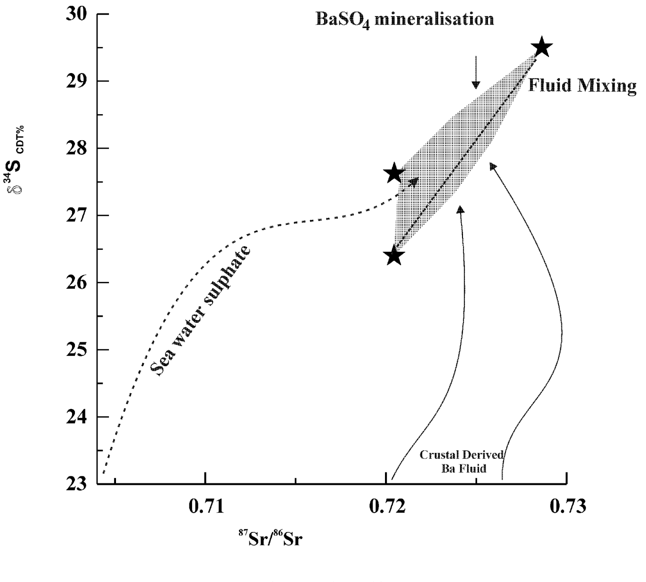

**Figure 3.** Bilinear plot of $d^{34}$S vs $^{87}$Sr/$^{86}$Sr values of the Tons valley barite; field of fluid mixing during initial deposition of barite is shown.

shares depositional and evolutionary history. Sulphur for the initial deposition of barite was probably supplied by sea water during Proterozoic. This may be related to early diagenesis of the host rock, which is also indicated by features like enclaves of barite in the host rocks and vice versa, their matching petrographic features and fluid characters[6]. Further, re-equilibration of the primary fluid due to high internal pressure > confining pressure, expresses decrease in the external pressure and an isothermal decompression uplift path[6], both for barite and its host rocks.

High values of $^{87}$Sr/$^{86}$Sr in the studied barite imply that strontium was supplied from highly radiogenic old crustal source rocks without any influence of magmatic rocks and marine volcanic activity. It is suggested that Ba was derived from the leaching of silicate minerals present in the protolith of the host rock, i.e. Banded Gneissic Complex[5]. Leaching of Ba from silicate minerals of the source area is plausible in view of the behaviour of Ba during fractional crystallization of magma, where Ba gets mostly confined to K-bearing minerals, such as feldspar and mica. Ba and K ions can replace each other at high $P$–$T$ conditions, as they are isostructural. Consequently, 400–10,000 ppm Ba is found in granite, and K-feldspar in granite may contain up to 6% Ba[19]. Hence, $^{87}$Sr/$^{86}$Sr and S-isotope signatures of the Tons valley barite present two distinct evidences. On this basis, we propose that the process of mixing of two fluids, viz. barium-rich crustal fluid and sea water sulphate, led to barite mineralization in the Tons valley (Figure 3). Such fluid mixing has also been interpreted by the study of primary inclusions in barite and host siliciclastics[6]. Primary inclusions in original coarse grains support mixing of two fluids with one having low temperature and low salinity than the other, thereby revealing cooling of the fluid along with its dilution. Features like bimodal grain fabric, deformation of cleavage plane in barite, fluid inclusion study, etc. suggest two stages of barite evolution: initial deposition and recrystallization. For the initial deposition of studied barite, both $^{87}$Sr/$^{86}$Sr and $d^{34}$S data point to crustal-derived barium and the Proterozoic sea water (sulphate) supplied sulphur.

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