

Stable isotope geochemistry of Early Cambrian Tal phosphorite of Krol Belt, Lesser Himalaya

A. Mazumdar
D. M. Banerjee

Department of Geology, University of Delhi, Delhi-110007, India

The Baliana, Krol and Tal Group of sedimentary rocks represent the Neoproterozoic- Early Cambrian sequence of the Krol Belt in the Lesser Himalaya. The Chert-Phosphorite Member of Tal Group constitutes the most important stratigraphic segment in this belt owing to a large deposit of phosphorite. This Member is exposed in the Nigalidhar, Korgai, Mussoorie and Garhwal synclines of the Krol belt. Stable isotopic data on phosphorites presented here are based on sampling carried out at Durmala and Maldeota sections of the Mussoorie syncline. The primary depositional features such as small-scale cross beddings, small scale ripple marks in grainstone phosphorites, intraclasts, ooides, microbial laminites and small domal stromatolites (Mazumdar, 1996) are suggestive of intertidal to shallow subtidal depositional settings for Chert-Phosphorite Member of the Lower Tal Formation. Rhythmic disposition of several episodes of shallowing upward cycle within 10 to 15 cm thick phosphate beds indicate very shallow water depositional environment with frequent changes in the

water depth. Presence of phosphate intraclasts, rip-off clasts and fragmentation of the stromatolitic fabric and their redeposition in the intercolumnar spaces are indicative of intermittent high energy conditions. Such gross textural features of the shallow marine depositional milieu are characteristic of most of the Late Proterozoic and Early Cambrian phosphorite deposits of the world, which make them distinctly different from younger phosphorites believed to have formed under relatively deeper water conditions. Carbonate fluorapatite (CFA) is the main phosphatic mineral in the Tal phosphorite. Minor quantity of dolomite/calcite and chert are the main matrix minerals other than detrital quartz, mica, sericite and clays. The organic content varies from <1% to 3%.

Stable Isotopic Results

Isotopic ratios of both carbon and oxygen were determined for the CO₂ obtained by reacting the powdered phosphorite samples in 100% phosphoric

TABLE 1. Carbon and oxygen isotopic values of Tal phosphorites

Sample name.	$\delta^{13}\text{C}_{\text{carb}}$ (‰)	$\delta^{18}\text{O}_{\text{carb}}$	Corg (%)	$\delta^{13}\text{C}_{\text{Corg}}$	Dd
SK6	-10.03	-10.35	1.55	-33.56	23.53
SK9	-7.43	-12.12	1.28	-33.12	25.69
SK1	-6.29	-12.54	0.92	-32.76	26.47
SK2	-11.4	-11.97	1.05	-33.0	21.6
SK4	-17.75	-11.18	1.43	-33.89	16.14
SK7	-8.83	-12.36	3.00	-34.5	25.67
DQ16	-4.53	-7.90	1.42	-28.18	23.65
DQ17	-5.43	-8.95	2.10	-32.31	26.88
DQ18	-7.13	-8.14	0.75	-33.35	26.22
DU6	-8.02	-13.400	1.56	-28.16	20.14
DU7	-7.43	-12.700	0.00	-32.6	25.17
DU8	-6.39	-10.520	1.62	-31.31	24.92
DU9	-6.02	-12.910	3.52	-30.18	24.16
DU4	-14.53	-23.270	0.95	-33.21	18.68
DU5	-7.36	-12.570	1.67	-28.92	21.56
DU10	-7.05	-12.250	3.10	-31.78	24.73
DU12	-7.66	-11.980	1.87	-28.63	20.97

Table 2. Sulphur isotopic values of pyrite in Tal phosphorite

Location	$\delta^{34}\text{S}$ (‰) range in pyrite	Pyrite type
Maldeota Mine	-5.8 to 45	spheroidal, microstromatolitic, replacing phosphate pellets, aggregates
Durmala Mine	-25 to 36.5	fragmental, microbial laminites, microstromatolitic

acid. $\delta^{13}\text{C}_{\text{carb}}$ values (Table 1) of bulk phosphorites belonging to Maldeota Mine (SK) section show maximum variation ranging from -6 to -17‰. The lightest $\delta^{13}\text{C}_{\text{carb}}$ is also observed in this section. Compared to this, $\delta^{13}\text{C}_{\text{carb}}$ of phosphorite belonging to Durmala Mine (DU and DQ) section show a smaller spread (-4 to -8‰) except for one sample with exceptionally low value. The underlying Nemakit-Daldynian /Late Neoproterozoic Krol dolomites have average $\delta^{13}\text{C}_{\text{carb}}$ value of -0.5‰. The $\delta^{13}\text{C}_{\text{org}}$ (Table 1) varies from -30 to -34‰ in both Maldeota and Durmala phosphorites. Some heavier values (-28 to -28.9‰) have also been reported. The variations in the $\delta^{13}\text{C}_{\text{org}}$ values may be attributed to intrabasinal changes in nutrient availability and productivity. Compared to $\delta^{13}\text{C}_{\text{org}}$ of the black shale and phosphorite the $\delta^{13}\text{C}_{\text{org}}$ of the underlying Krol dolomite is around -28‰. The $\delta^{18}\text{O}$ values (Table-1) show limited variation (-10 to -13‰) in the phosphorites of both Durmala (DU) and Maldeota mine (SK) sections except one abnormally low value. DQ section shows comparatively heavier value (-7 to -8‰).

Gross temperature estimate based on kerogen-colour and illite crystallinity studies (Mazumdar, 1996) supports the fact that the organic matter in the Tal phosphorite has not been thermally altered and is well preserved. Consequently, the $\delta^{13}\text{C}_{\text{org}}$ values did not shift substantially from their primary isotopic composition. It can therefore be assumed that the negative $\delta^{13}\text{C}_{\text{org}}$ excursion as high as -4 to -6‰ in the Tommotian phosphorite (Banerjee *et al.*, 1997) relative to the underlying Krol dolomite suggests an equivalent modification of the basinal water composition ($\text{CO}_{2(\text{aqueous})}$) during the early Cambrian ocean mixing process which brought the deeper P , ^{12}C and other trace element rich waters on to the shallow carbonate platform. The average $\delta^{13}\text{C}_{\text{carb}}$ value (-8.9‰) of the Tal phosphorite (compared to 0 to -0.5‰ in the underlying Krol dolomite) is skewed due to few highly negative values. In fact, most of the values are heavier than the average value of ~ -8.9 ‰. The $\Delta\delta$ ($\delta^{13}\text{C}_{\text{carb}} - \delta^{13}\text{C}_{\text{org}}$) value is an indicator of the

relative modification of $\delta^{13}\text{C}_{\text{carb}}$ by organic decomposition. The $\Delta\delta$ value decreases with increase in the lighter carbon (^{12}C) in the phosphorite. In view of the fact that the basinal water was already depleted in ^{13}C (negative excursion of -4 to -6‰) at the time of deposition of the Lower Tal phosphorite, further negative shift of 3 to 4‰ in the $\delta^{13}\text{C}_{\text{carb}}$ of phosphorite probably bears the imprint of suboxic diagenetic modification (McArthur *et al.*, 1986). In other word, the $\delta^{13}\text{C}_{\text{carb}}$ values of the phosphorite is partly due to basinal water modification and partly due to suboxic-early diagenetic processes in the organic rich phosphate mud. Very high negative shift in two samples (upto -17‰), on the other hand indicates effects of sulphate reduction during sediment burial. In most cases the negative carbon isotopic signature of the phosphorite, acquired during early-diagenesis remained virtually unmodified (-6 to -7‰).

Pyrite is present ubiquitously in the Tal phosphorite as thin to thick discontinuous layers, cross-cutting veinlets, pyritised algal mats, phosphate clasts, granules and shelly fragments. $\delta^{34}\text{S}$ measurements (Table-2) show a large spread of values ranging from -25‰ to +45‰. i.e. a spread of 70‰ (Banerjee *et al.* 1997, p.192) indicating pyrite formation in sulphate reducing to methanogenic diagenetic environments.

It is concluded that while phosphatisation took place under exclusively suboxic non-sulphate reducing conditions, pyritisation began only when phosphate layer entered the zone of sulphate reduction.

References

- Banerjee, D.M., Schidlowski, M., Siebert, F. and Brasier, M.D. (1997) *Paleogeogr., Paleoclimatol., Paleocol.*, **132**, 183-94.
- Mazumdar, A. (1996) *Unpublished Ph.D. Thesis*, University of Delhi, Delhi, 246p.
- McArthur, J.M., Benmore, R.A., Coleman, M.L., Soldi, C., Yeh, H.W. and O'Brien, G.W. (1986) *Earth Planet. Sci. Lett.*, **77**, 20-34.