

smaller size (consequently, a better steric accessibility) – appear to be crucial for the molecules to form an energetically favourable complex with the receptor which would interfere with the subsequent reactions taking place in the receptor.

The computational results of this theoretical MESP analysis on the different conformers of acetaldehyde, nitrous acid and hydroxylamine indicate that three factors – (i) the magnitude of the deepest negative potential, (ii) a large 'optimum' negative potential zone and (iii) small size – would contribute largely towards their biological activity. The MESP analysis may thus be used as a tool to determine the degree of mutagenic capacity *vis-à-vis* deprotonating as well as deaminating abilities of these molecular mutagens.

Although electrostatic potential patterns shown in this study can offer a rich informative description about the capacity of the molecules to generate stereoelectrostatic forces, they fail to describe their ability to generate hydrophobic bonds and dispersion interactions. Therefore, the MESP profiles in the present investigation would reveal only the stereoelectronic components of intermolecular recognition forces. Thus, further sophisticated calculations including solvent effects are required to prove or disprove the proposed reasons for the biological potency of the molecules.

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## Record of 1.66-Ga-old marine oxido-reducing conditions from an unusual Sargipali Pb–Cu deposit (India): A preliminary appraisal through petrogenesis

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In the Proterozoic marine reducing environment the evidence of oxidizing condition from petrogenesis of some unusual metamorphic rocks like calcite-brucite, quartz-diopside and diopside-rich skarn has not been reported. The results of this contribution imply that, despite complete alteration of their precursor sedimentary rock composition, there is little change in the original behaviour of the rare-earth elements. Primarily on this basis, information about the changing Proterozoic oxidation state in the reducing seawater environment is put forth on the basis of Ce anomaly. The observation may be significant in view of the worldwide rarity of data concerning oxido-reduction characteristics of the Proterozoic marine realm. In addition, a new documentary evidence for  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  isotopic depletion in the marble developed due to metamorphism of the pure dolomite rock under at least 600°C at 6 kb *PT*-conditions is also brought out. Until now it was generally believed<sup>1</sup> that the pure carbonate rocks do not show a net lowering of these isotopes under metamorphic conditions.

THE 1.66-Ga-old stratiform Sargipali sulphide deposit<sup>2</sup> of the Gangpur Group, eastern India (Figure 1), is a

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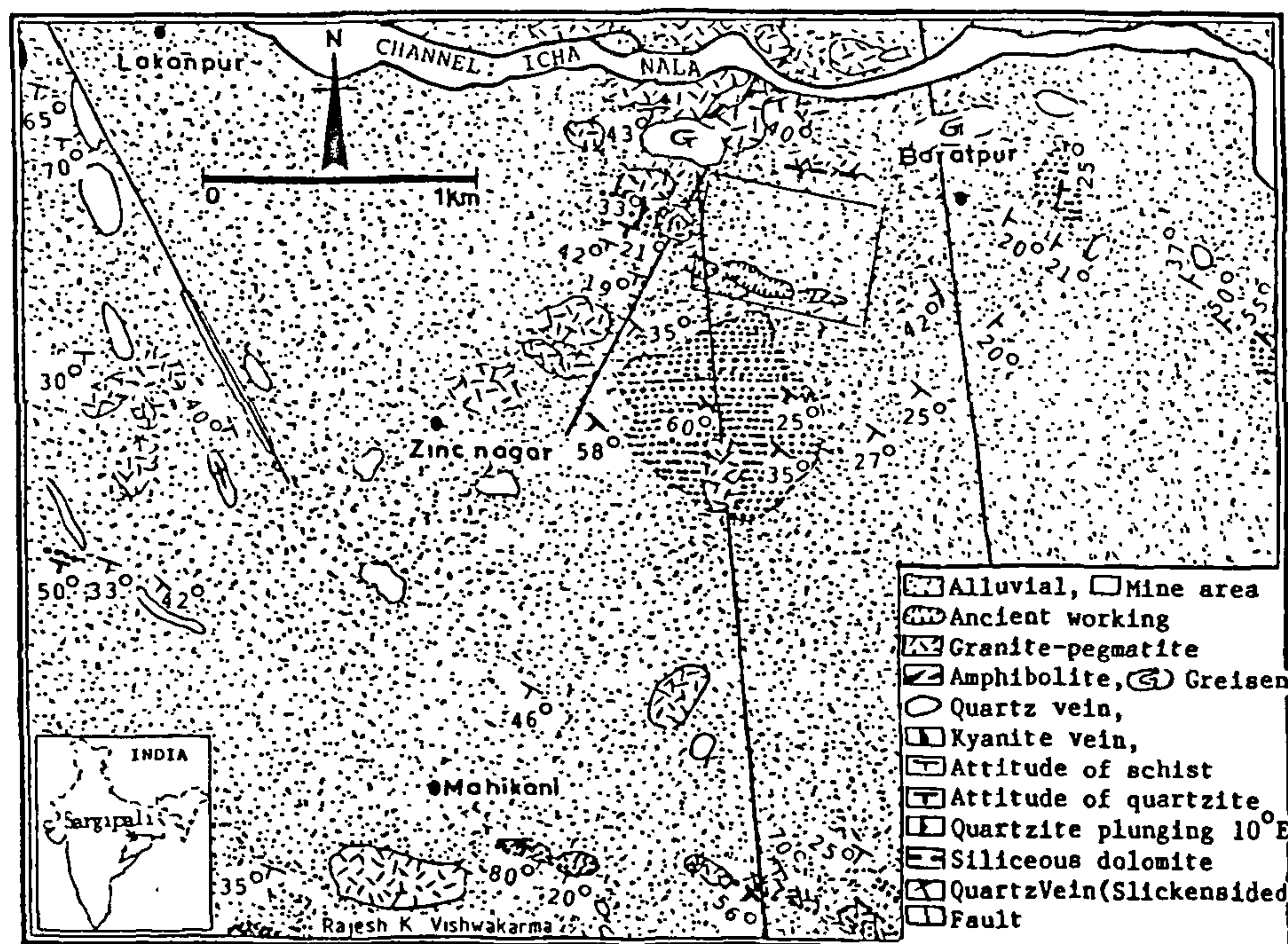


Figure 1. Geological map of the Sargipali Pb-Cu mine area. Inset shows the location of the study area.

syngenetic deposit which is formed due to sedimentary exhalative activity in response to the slow-spreading rift system<sup>3</sup>. Palaeoenvironmental study indicates that the area represents intertidal to supratidal marine flat environment<sup>3</sup>. This interpretation is based on polymictic metaconglomerate and current bedded structures (within meta-arenaceous lithounit), intercalations of quartzite, chert and carbonate skarn (within meta-argillaceous lithounit) and laminae of quartz-mica-chlorite within carbonate lithounit (Figure 2). These rocks are not included in the previous<sup>5</sup> stratigraphic scheme. Another interesting feature of the Sargipali deposit is the unusual Pb-rich mineralization with Cu association, which took place during deposition of the predominantly shaly sediments<sup>4</sup> (now represented by quartz-mica-chlorite schist, Figure 2) under reducing seawater environment. Lack of any contemporaneous oxidized facies around the ore body and the host quartz-mica-chlorite rock, the presence of thin pyrrhotite-rich bands in the deep mine levels, and the presence of graphite laminae in the ore and the gangue (Figure 3) collectively contribute to the idea of a reducing seawater environment. The present contribution, based on the study of petrogenesis of three rocks like marble, quartzite and skarn (which occur in the field as minor and impersistent lithounit), however, shows an evidence of oxidized environment during the

formation of Proterozoic rocks in the area of study. Further, a geochemical evidence for the reducing condition is also being reported. Obviously, these findings are novel, since such type of data concerning this Proterozoic period remain rare worldwide.

The proposed programme has greatly benefited from the author's earlier work<sup>4</sup>, in which a sufficient number of rock samples from various lithounits of the Sargipali area were analysed with respect to rare-earth elements (REEs). Out of these, three rocks, viz. marble, skarn and quartzite (which happen to be unusual on account of the mineral association presented in the following petrographic description), display a well-defined Ce anomaly. Therefore, the same is being reported and discussed as preliminary appraisal.

Furthermore, it may be imperative to point out that, although the analysed samples may not appear to be sufficient from statistical point of view, the REE trends represented by these analyses are quite logical and tenable in the light of the available literature. Hence, their utility is warranted in view of the fact<sup>6</sup> that sometimes, with the help of trace and rare-earth elements, geochemical modelling is possible even with one sample. With this assumption, a discussion on the above geochemical characteristics is made. But before this it is necessary to evaluate if the REE patterns of these



	LITHOSTRATIGRAPHIC UNIT	LITHOLOGY	THICK- NESS (m)
GANGPUR GROUP (PROTEROZOIC)	IGNEOUS INTRUSIVES	DOMINANTLY GRANITE-PEGMATITE, AND MAFIC IGNEOUS ROCK	
	CALCAREOUS ROCK	SILICEOUS DOLOMITE, MARBLE AND LIME- STONE WITH QUARTZ-MICA-CHLORITE SCHIST LAMINAE	~200
	ARGILLACEOUS ROCK	QUARTZ-MICA-CHLORITE SCHIST WITH INTERCALATIONS OF QUARTZITE(==) AND SILICEOUS DOLOMITE (---)	150
		QUARTZ-MICA-CHLORITE SCHIST WITH ORE LODE (—), AND INTERCALATIONS OF CARBONATE SKARN (---), CHERT (≡), QUARTZITE (==) AND TOURMALINITE(---)	
		BIOTITE-GARNET/TOURMALINE SCHIST. PHYLLITE.	
		MICA SCHIST.	160-200
	ARENACEOUS ROCK	QUARTZ-SERICITE, INTRAFORMATIONAL METACONGLOMERATE AND QUARTZITE.	500-700

Figure 2. Generalized lithostratigraphy of Sargipah mine area (modified after Kar Ray<sup>5</sup>).

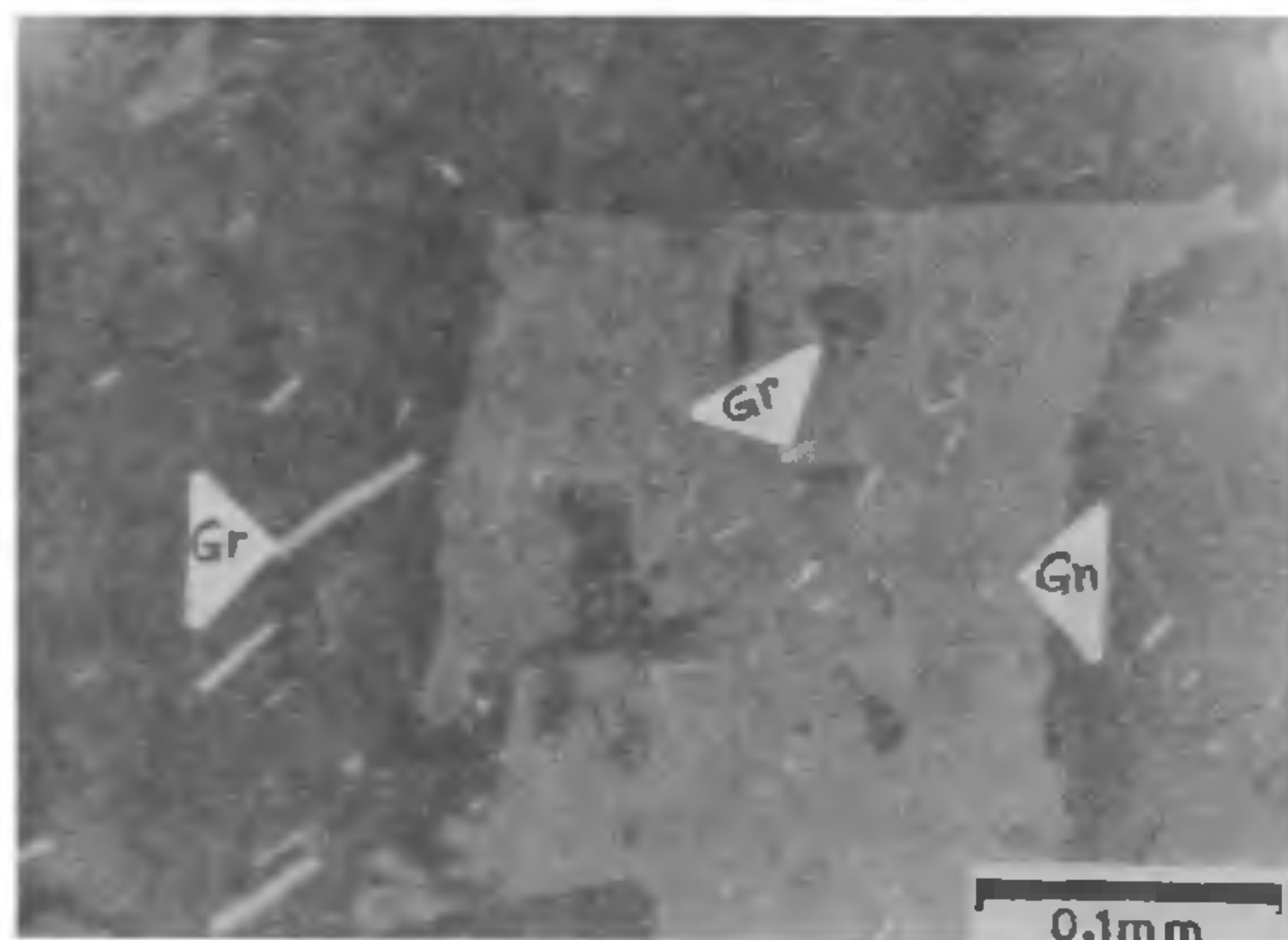


Figure 3. Occurrence of graphite in galena and gangue. Crossed polars. Specimen in oil. Gn = Galena, Gr = Graphite.

rock samples are at all representative of the original conditions of sedimentation, because the rocks have experienced multiple deformation, and also recrystallization over *PT* conditions of at least 600°C at 6 kb (ref. 4). To start with (i.e. the originality of REE pattern), the petrographic study is taken up. The quartzite sample,

which has been collected from 'Mahikani' Hill, 4.6 km SSW to the prospecting mine (Figure 1), contains quartz and diopside as the major constituents; tremolite and zircon are minor while epidote is in the trace amount. Diopside occupies the intragranular space of quartz (Figure 4), containing noticeable amounts of zircon inclusions. Most likely, diopside in this rock represents a metamorphic equivalent of the initial impure carbonate which was mixed with initial quartz grains. It may, therefore, define a pure quartz sandstone, since in these rocks impure carbonate can occur as an irregular, scattered mass<sup>7</sup>. A provenance of this rock, as indicated by the total absence of feldspar and micas, could then lie chiefly with the quartzose sediment and/or the low-grade metamorphics of possibly quartzite. Petrographic study of *skarn* rock, which occurs as a thin laminae within quartz-mica-chlorite schist at 180 MRL of the underground mine reveals a calc-silicate mineral assemblage defined by diopside-tremolite-hornblende-chlorite-actinolite-calcite  $\pm$  sphene. Here diopside is most abundant and, therefore, it can be a derivative of impure carbonate metamorphosed to amphibolite facies grade<sup>8</sup>. The petrographic study of *marble* (which is collected from its 2-3 inches thick concordant band in association with phyllite of the meta-argillaceous lithounit of the under-



ground mine at 120 MRL) reveals the groundmass of calcite to contain sometimes a minor patch of fibrous brucite. As a rule, this points to an original pure dolomite that upon metamorphism got decomposed and recrystallized to calcite and periclase with escape of  $\text{CO}_2$  (ref. 9). In the presence of  $\text{H}_2\text{O}$ , however, periclase is transformed to brucite ( $\text{MgO} \cdot \text{H}_2\text{O}$ ). This assessment, therefore, clearly agrees with the high MgO content of the analysed sample (Table 1). If it is so then the observed role of metamorphic decarbonation reaction is likely to disturb the reliability of the more sophisticated analytical data like  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  isotopes and REEs. Particularly, the isotopes of both  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  show a low value of  $-18.8$  and  $-11.01\text{‰}$ , respectively (mean of three samples with respect to PDB), because  $\text{CO}_2$  liberated could have been enriched in  $\delta^{18}\text{O}$  as well as  $\delta^{13}\text{C}$  relative

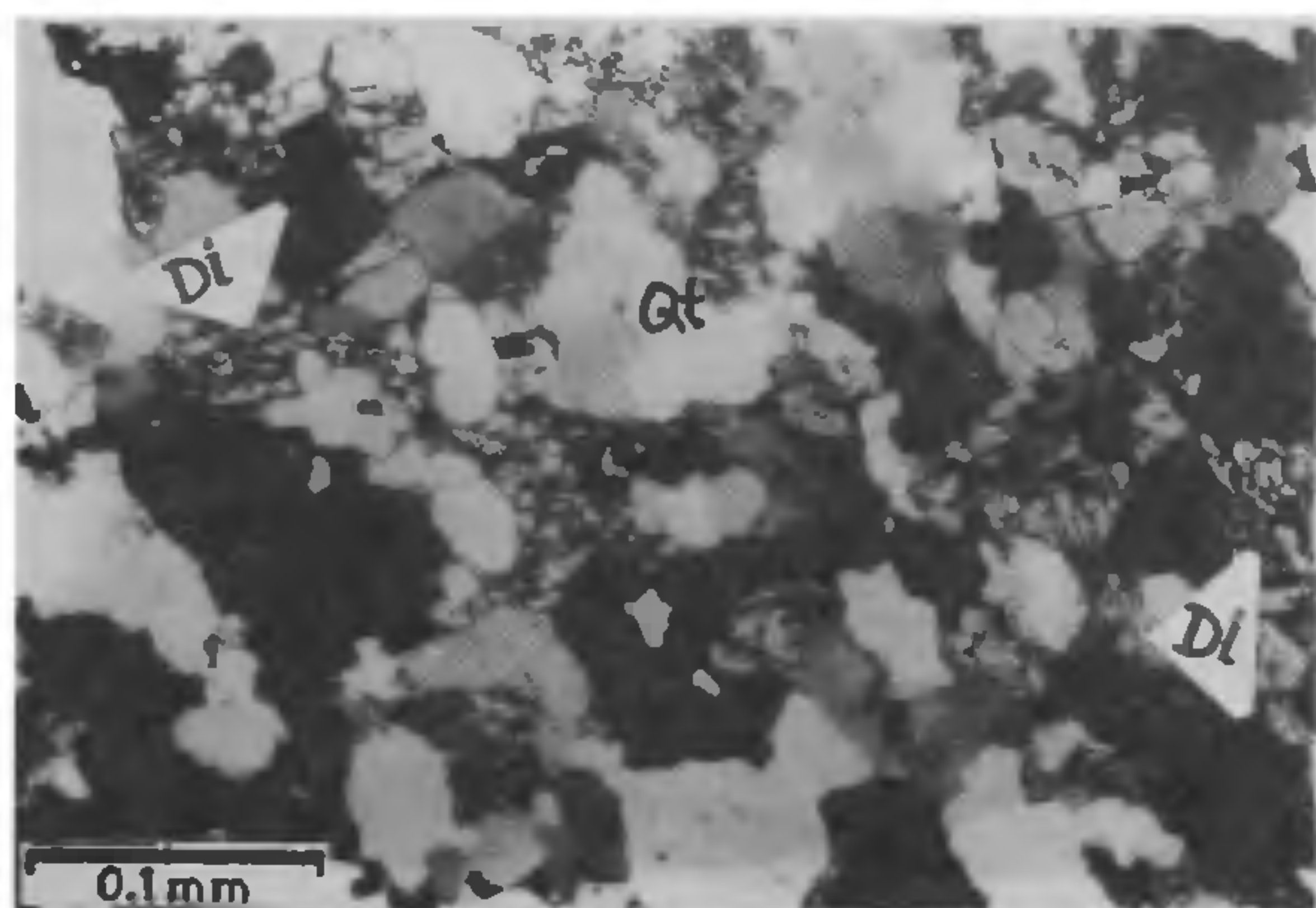


Figure 4. Photomicrograph of a rare quartzite showing diopside in the intragranular space of quartz grains. Crossed polars. Qt = quartz, Di = diopside.

Table 1. Major oxide composition in quartzite, skarn, marble and phyllite in (wt%)

	Quartzite	Skarn	Marble	Phyllite
$\text{SiO}_2$	82.74	48.73	1.02	60.12
$\text{TiO}_2$	0.03	0.07	0.00	0.53
$\text{Al}_2\text{O}_3$	0.54	6.02	0.04	18.40
$\text{Fe}_2\text{O}_3$ (T)	3.42	4.39	0.00	8.19
CaO	7.25	24.80	67.25	0.91
MgO	3.23	11.93	8.98	3.08
$\text{Na}_2\text{O}$	1.02	2.21	0.08	0.60
$\text{K}_2\text{O}$	0.39	0.35	0.01	3.62
MnO	0.12	0.42	0.37	0.23
$\text{P}_2\text{O}_5$	0.56	0.64	0.03	0.05
LOI	0.82	0.13	20.72	4.72
Total	100.10	99.69	98.50	100.45

to the carbonate<sup>10</sup>. On the other hand, compatibility of the REE data, particularly in relation to the precursor rock, is also a subject of examination, as follows in the ensuing discussion.

REE concentrations in the above rocks, obtained by inductively coupled plasma mass spectrometry with a precision of better than 7% relative standard deviation, are plotted as a REE pattern (Figure 5). Quartzite in this figure is rich in REE. This behaviour when considered in conjunction with the steep fractionated REE pattern may well represent a detrital origin of the rock. If this is true then, on the basis of the predominance of quartz, the rock can be conveniently assigned to sandy precursor; it is plausibly sandstone, because these are enriched in all REEs relative to chondrites<sup>11,12</sup>. Other samples, viz. marble and skarn, however, display depleted total REE with enriched heavy REE pattern (Figure 5). This behaviour not only corresponds to that of sediment but also suggests<sup>11</sup> that the rock is formed by the chemical precipitation process in marine environment. The reason behind the idea of marine hydrogenous origin lies in the fact that the above behaviour of REE is reminiscence of a low total concentration of REE with slight enrichment of heavy REE in seawater. In addition to this, it also appears that, although the rocks have evolved due to contact metamorphism, the magmatic water from the granitic stock did not introduce any large amount of REEs into the original rock compositions<sup>13</sup>. So, all these assessments may invariably support a general notion: the behaviour of REE during diagenesis and/or metamorphism indicate that there is little change in either the absolute abundances or the relative patterns.

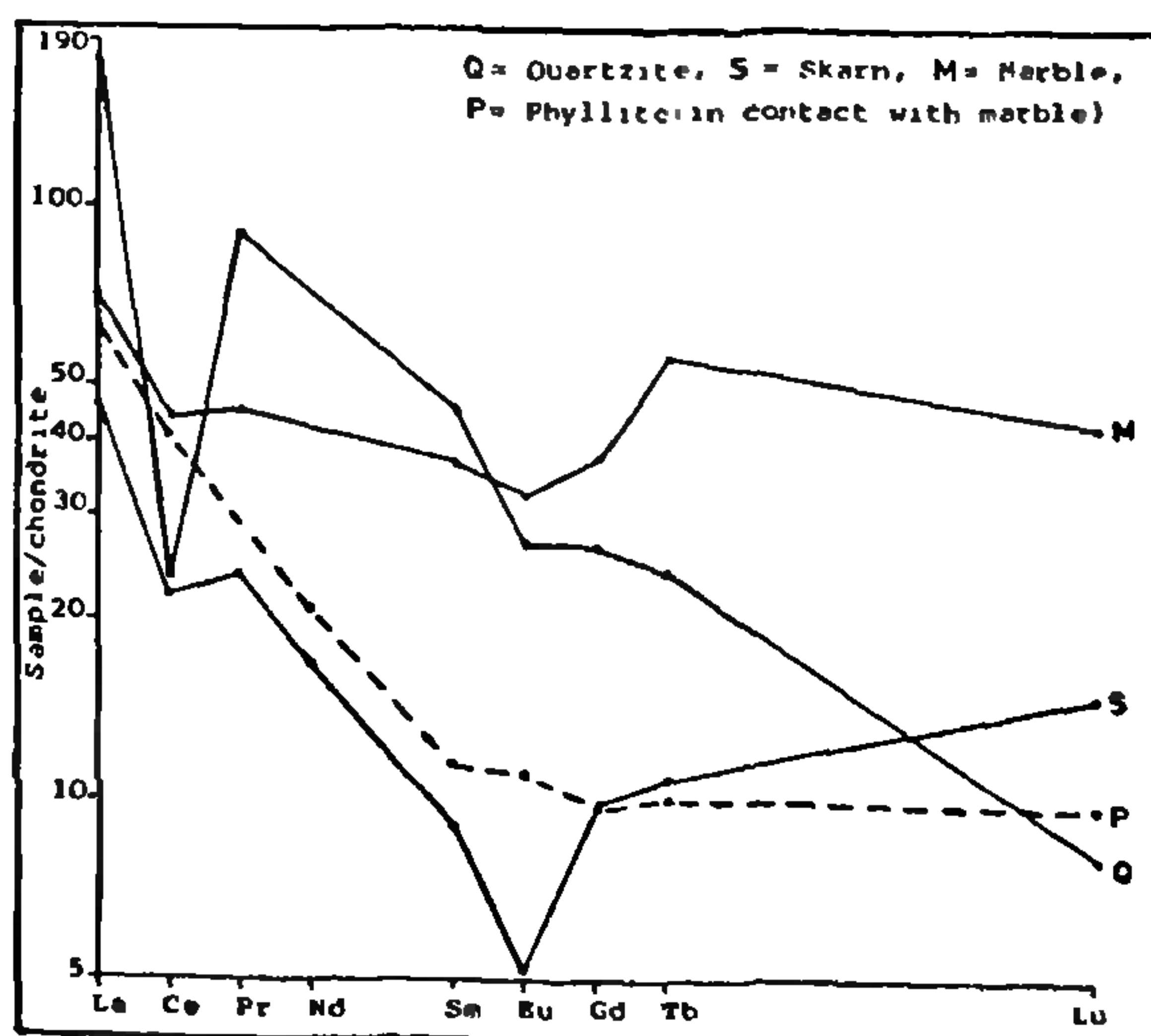


Figure 5. REE distribution pattern showing negative Ce anomaly in Sargipah quartzite, skarn and marble



Nevertheless, in fulfilment of the reliability of the data, it is needed to bring out the factor governing minor Eu depletion in the studied samples (Figure 5). Critical to this, an effective way for removing Eu could have been the precipitation of  $\text{Eu}^{2+}\text{SO}_4$ . Such a mechanism is capable of removing most of the Eu while leaving most of the other REE<sup>14</sup>. If it is so, then at least most of the other samples formed in reducing conditions (e.g. quartz–mica–chlorite schist shown in figure 13 of Vishwakarma<sup>4</sup>) would have also yielded Eu depletion by this method. On the contrary, all these samples show positive Eu anomaly along with the steep fractionated REE pattern, and the features are actually, 'supplementary' evidence to charnockite provenance<sup>4</sup>. Here it may be annotated that by virtue of an evidence of the least Eu enrichment in the phyllite sample (Figure 5), which contains disseminated graphite, it cannot be invoked straightaway that the reducing conditions are prone to the formation of detectable Eu anomaly. Over and above, it is also not possible to propose removal of Eu anomaly due to remelting<sup>15</sup> or due to the influence of metamorphic fluid–rock interaction<sup>16</sup>. Likewise, the introduction of an oxidizing environment too has not a discernible effect on the behaviour of Eu<sup>17</sup>. Therefore, it seems that Eu anomalies in the samples of this study actually reflect an inherent property of their precursor. With this there remains no doubt that the REE patterns of the rocks are fairly representative of original sedimentation, and hence the observed feature of negative Ce-anomalies may be useful in providing an insight into the marine water condition during the formation of the rock<sup>12, 17–20</sup>. If this water is in an oxidizing condition, a smaller fraction of Ce will be trivalent, therefore resulting in Ce-depleted water condition and in turn Ce-depleted REE pattern in the marine sediments<sup>19</sup>. This scenario could have set in by the oxidation of  $\text{Ce}^{3+}$  under conditions of strong chemical complexation. Particularly, carbonate complexes of  $\text{Ce}^{4+}$  are the ones that control Ce in marine water (Möller, 1992, personal communication). Alternatively, according to experimental studies<sup>21, 22</sup>, it is the oxidation of  $\text{Ce}^{3+}$  into  $\text{CeO}_2$  that causes Ce deficiency. This, therefore, corroborates the original idea of Goldberg<sup>18</sup>. The present study also reckons this observation in the light of the following. Phyllite (Figure 5) and quartz–mica–chlorite schist samples (Figure 13 of the earlier study<sup>4</sup>) both indicate a reducing environment of formation. So, for the obvious lack of oxygen, Ce removal by formation of  $\text{CeO}_2$  could not take place, and as a result there remains normal La/Ce ratio, that

is to say, normal REE pattern (Figure 5). Furthermore, the intensity of Ce anomaly observed in the present study is variable. Most likely, it is attributable to the quantum of the small fraction of  $\text{Ce}^{3+}$  which is left in an overall oxidizing marine condition.

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