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## Ca-Ba-Sr carbonates from metamorphosed manganese deposits of the Sausar group, India, and their petrological significance

SOLID solutions in natural orthorhombic carbonates have potential petrological significance in constraining equilibrium relations. Additionally, coexisting orthorhombic and rhombohedral carbonates have a good potential as geothermobarometers (Essene, 1983). Orthorhombic carbonates are known from sedimentary rocks (Mitchell and Pharr, 1961; Harder, 1964) and metasomatic/hydrothermal ore deposits (Deer *et al.*, 1962; Sundius, 1965; Speer, 1983, and the references cited therein) but have so far not been characterized in metamorphic rocks. The *P-T* net of Froese (1970), based on the experimental data of Chang (1965) in the system  $\text{CaCO}_3\text{-SrCO}_3$ , therefore, cannot be tested in metamorphic rocks.

When applied to sedimentary carbonate pairs, this net predicts unrealistic temperatures (Essene, 1983).

Against this background, we present chemical characteristics of several coexisting Ca-Ba-Sr-Mn carbonates from the metamorphic assemblages of the Precambrian Sausar Group, India, and discuss their petrological significance. The carbonates occur in metamorphosed carbonate-facies manganese deposits at Netra, Balaghat district, India. The manganese deposits contain braunite and jacobite in addition to Mn carbonates. Textural relations indicate that these oxides evolved through prograde decarbonation-oxidation reactions of manganese carbonate sediments

Table 1. Representative chemical analyses of coexisting carbonate minerals from the Netra area. Total Mn and Fe are given as MnO and FeO respectively. B, barytocalcite; S, calcian strontianite; M, manganocalcite; C, calcite.

Sample No.	N 1				N 1 A				N 1 B			
	B	S	C	M	B	S	C	M	B	S	C	M
FeO	—	—	0.12	—	—	—	0.02	—	—	—	—	—
MnO	0.12	0.01	0.41	10.21	0.41	—	0.50	10.60	0.29	0.04	0.33	10.96
MgO	0.02	—	0.12	0.41	0.04	—	0.03	0.34	—	—	—	0.37
CaO	19.30	10.76	53.82	43.88	19.00	11.37	49.19	41.87	19.37	8.68	54.96	41.78
BaO	50.63	5.51	0.78	0.69	49.76	5.40	0.76	0.48	49.03	7.04	0.54	0.47
SrO	0.49	50.27	0.96	3.46	1.78	49.36	0.85	3.66	2.69	52.23	0.46	3.97
Oxygen (3)												
Fe	—	—	.002	—	—	—	—	—	—	—	—	—
Mn <sup>2+</sup>	.002	—	.005	.148	.008	—	.004	.158	.006	.001	.015	.163
Mg	.001	—	.003	.01	.001	—	—	.009	—	—	—	.01
Ca	.505	.269	.980	.803	0.493	.266	.989	.792	.497	.219	.961	.784
Ba	.485	.05	.003	.005	0.472	.050	.003	.003	.460	.065	.012	.003
Sr	.007	0.68	.004	.034	0.025	.685	.003	.037	.037	.715	.012	.04

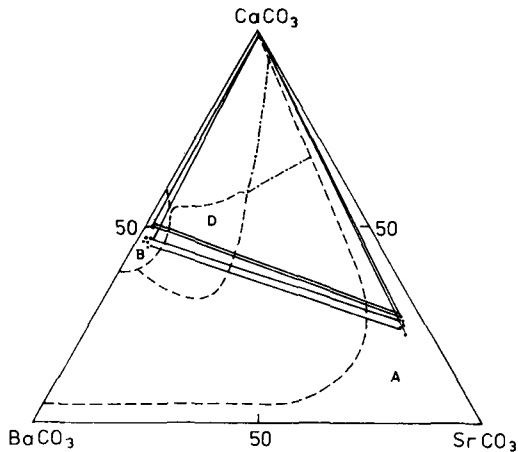


Fig. 1. Composition of the co-existing Ca-Ba-Sr carbonates in the system  $\text{CaCO}_3\text{-BaCO}_3\text{-SrCO}_3$  metamorphosed at 6 kbar, 660°C. Superimposed are the experimentally determined phase relations at 10 kbar, 550°C (Chang, 1971). Dashed lines, fields of the carbonates: A, aragonite-type structure; B, barytocalcite; D, disordered calcite structure. Dotted-chain line: three-phase field.

Table 2. Representative chemical analyses of apatite (A) and baryte (B) from the Netra area. In sample N\*\* 1, carbonate is not present.

Sample No.	N - 1		N - 1A		N** 1	
	A	B	A	A	A	A
MnO	0.08	0.28	0.17	0.48		
MgO	—	0.04	—	—		
CaO	52.37	—	51.82	41.95		
BaO	—	62.04	—	0.10		
SrO	3.24	0.51	3.41	16.04		
P <sub>2</sub> O <sub>5</sub>	41.45	—	41.78	39.34		
Mn <sup>2+</sup>	.006	—	.012	.037		
Mg	—	—	—	—		
Ca	4.81	—	4.751	4.073		
Ba	—	—	—	.004		
Sr	.161	—	.169	.843		
P	3.008	—	3.027	3.018		

during metamorphism (Bhattacharya *et al.*, 1988; Dasgupta *et al.*, 1989a,b). Garnet-biotite thermometry in the associated metapelites indicates metamorphism at c. 660°C at an estimated pressure of 6 kbar (Roy *et al.*, 1986).

The mineral assemblage discussed here is braunite + jacobsite ± hausmannite + baryte + apatite + clinopyroxene (manganian acmite-diopside solid solution) + manganian calcite + calcite + barytocalcite + calcian strontianite ± hematite. All the types of carbonates form polygonized grains and are in textural equilibrium with the associated apatite, silicates and oxides. Inclusions of the carbonates in the oxides and symplectitic intergrowths between these phases are common textural features. Barytocalcite and calcian strontianite are often intergrown and the former occurs as lamellae in the latter.

Chemical compositions of the four types of carbonates and the associated phases were determined by a JEOL-JXA 733 EPMA and the results are given in Tables 1 and 2. Manganian calcite contains 15–16.5 mole %  $\text{MnCO}_3$  and 3–4 mole %  $\text{SrCO}_3$ . Barytocalcite contains 46–48.5 mole %  $\text{BaCO}_3$  and 1–4 mole %  $\text{SrCO}_3$ . Calcian strontianite contains 61–71, 5–6.5 and 24–28 mole % of  $\text{SrCO}_3$ ,  $\text{BaCO}_3$  and  $\text{CaCO}_3$  respectively. Calcite is nearly pure  $\text{CaCO}_3$ . Apatite coexisting with Ca-Ba-Sr carbonates contains 1–7% SrO but that associated with clinopyroxene or oxides may contain up to 16 % SrO (Table 2). The preference for Sr at the ambient *P-T* condition of metamorphism is carbonate > apatite ≥ baryte. In the absence of carbonates, Sr is strongly partitioned to apatite.

Although it was not possible to characterize the structural types of the carbonates, the phases enriched in Ba and Sr can be taken as orthorhombic on crystallochemical considerations (cf. Essene, 1983; Speer, 1983). On the same grounds, the Ca-Mn carbonate is rhombohedral (Goldsmith, 1983). The compositions of coexisting calcite, calcian strontianite and barytocalcite define the miscibility gap in the  $\text{CaCO}_3\text{-BaCO}_3\text{-SrCO}_3$  system (Fig. 1) at the ambient *P-T* ( $\approx 6$  kbar, 660°C) of metamorphism. The three phase region at this *P-T* is defined by the phases  $\text{CaCO}_3$ ,  $(\text{Ca}_{0.27}\text{Ba}_{0.05}\text{Sr}_{0.68})\text{CO}_3$  and  $(\text{Ca}_{0.50}\text{Ba}_{0.47}\text{Sr}_{0.03})\text{CO}_3$  which is quite distinct from that defined by the phases  $\text{CaCO}_3$ ,  $(\text{Ca}_{0.72}\text{Ba}_{0.02}\text{Sr}_{0.26})\text{CO}_3$  and  $(\text{Ca}_{0.56}\text{Ba}_{0.24}\text{Sr}_{0.20})\text{CO}_3$  at 10 kbar and 550°C (Chang, 1971). A notable decrease in the solubility of Ca in strontianite with decrease of pressure is evident. This trend is corroborated by the presence of low-Ca strontianites in sedimentary rocks (Mitchell and Pharr, 1961; Harder, 1964). Fig. 1 also shows that there is a concomitant

decrease in the solubility of Sr in Ba-carbonate with decreasing pressure.

The compositions of the coexisting calcite and strontianite considered in the  $P$ - $T$  net of Froese (1970) give an unrealistic temperature estimate. The presence of only 5 mole %  $\text{BaCO}_3$  in the latter cannot account for such an erratic estimate. Therefore, the geothermobarometer in the system  $\text{CaCO}_3$ - $\text{SrCO}_3$ , based on extrapolation of thermodynamic parameters from experimental data at high pressures, does not work in the  $P$ - $T$  regime of metamorphism. Additional experimental data at lower pressures, consideration of non-ideal mixing between Ca and Sr and more compositional data on natural assemblages in metamorphic rocks that equilibrated under varying  $P$ - $T$  condition are necessary to resolve this problem.

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