

A B S T R A C T

Precambrian non-calcareous manganeseiferous sediments of India associated with pelitic and psammitic rocks subjected to chlorite- to sillimanite-grade conditions of regional metamorphism have been examined in details with a view to determining the nature of mineralogical and chemical equilibrium attained in them.

Based on a series of idealized mineralogical reactions compatible with the recorded assemblages in the system Mn-Fe-Si-O, for many of which there is unambiguous textural evidence in the rocks, a combined schematic petrogenetic grid which is consistent with topological and thermodynamic considerations and valid for green schist to amphibolite facies, and probably also ^{for} granulite facies, condition of metamorphism has been constructed.

The petrogenetic grid, coupled with the mineralogical and textural evidence present in the manganeseiferous assemblages and the enclosing rock formations indicate that 1) the mineralogical reactions attending regional metamorphism of the manganeseiferous sediments buffered the composition of the coexisting fluid phase, 2) due to the closed nature of the system as a whole and also due to lack of communication between the different parts thereof, local variations in the initial proportions of the non-volatile to volatile phases and their compositions led to the development of contrasting sequences of mineralogical reactions and, therefore, f_{O_2} - T gradients even within the same metamorphic grade, and



3) rhodonite developed as a prograde reaction product in the garnet to sillimanite grade conditions was converted to rhodonite-pyroxmangite mixture/intergrowth during cooling.

New chemical data on twentysix braunite, twentyone jacobsite and twentysix rhodonite-pyroxmangite intergrowth, separated from these rocks have elucidated many important chemical relations existing in each of these three phases and also between the coexisting mineral pairs.

In braunite - 1) the concentration of silicon deviates little from the ideal value of one cation per twelve oxygen in the structure, 2) aluminium appears to be partitioned between the tetrahedral and the octahedral positions, and 3) the ferric iron content varies systematically with changes in the coexisting mineralogical assemblage and bulk rock chemistry and also, in general, increases with increasing grade of metamorphism.

Jacobsite, devoid of any exsolved hausmannite lamellae, becomes progressively enriched in magnesium and depleted in iron component with increasing grade, but its manganese content remains restricted within a small range. Its composition also varies regularly with changing mineralogy and bulk rock chemistry. The volume relations observed in the natural, homogeneous ternary jacobsite solid solution series - $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ (Mt) - $\text{MgO} \cdot \text{Fe}_2\text{O}_3$ (Mgf) - $\text{MnO} \cdot \text{Mn}_2\text{O}_3$ (Hs) - indicate a negative excess volume of mixing around - and a volume minimum at - approximately $\text{Mt}_{21} \text{Mgf}_{37} \text{Hs}_{42}$ composition; probably, this explains the restricted nature of jacobsite composition in regard to its manganese concentration, due to a tendency towards compound formation.

The 'MnSiO₃' phase is invariably a mixture/intergrowth of rhodonite and pyroxmangite. The Ca/(Mg+Fe) ratio of this mixture/intergrowth is more than 1 : 3 in every case and indicates that initially in garnet to sillimanite assemblages the phase crystallized to rhodonite and later inverted to pyroxmangite. Depletion of Mn, Fe and enrichment of Ca, Mg in rhodonite in association with hematite or jacobsite suggest that occasionally oxidative equilibria have been important. Otherwise, in general, there is a progressive increase in Ca + Mg + Fe²⁺ content of rhodonite with increasing grade. Rhodonite to pyroxmangite inversion indicated by the ratio $I_{Rh(21\bar{2})}/I_{Pxm(03\bar{2})}$ is incomplete in all the cases; concentrations of Ca, Mg and Fe in the phase and also the temperature of equilibration seem to have significantly controlled the degree of inversion. The inversion is most facilitated for the inferred composition Mn_{81.6} Ca_{11.5} Mg_{2.7} Fe_{4.2}. Away from this composition and within the chemical range considered, rhodonite is more stabilized relative to pyroxmangite.

The Mn³⁺ distribution in the braunite-jacobsite pair with and without rhodonite is dependent on the concentrations of Mn³⁺ and Fe³⁺ in both the phases and also shows systematic variation with grade of metamorphism.

In the jacobsite-rhodonite pair without associated braunite -
 1) Mn²⁺ distribution is dependent on the Mn²⁺ concentration in both the phases and also on Mn²⁺/Ca ratio in rhodonite, 2) Ca distribution is dependent on the concentrations of Mn²⁺ and Ca in both the phases, 3) Fe²⁺ distribution is dependent on the

concentration of Fe^{2+} and Mg/Fe^{2+} in rhodonite, and 4) Mg distribution is dependent on the Mg/Mn^{2+} ratio in jacobsite and Mg/Fe^{2+} ratio in rhodonite. In the braunite bearing jacobsite-rhodonite pair - 1) Mn^{2+} distribution is dependent on Mn^{2+}/Ca ratio in rhodonite and Mg and Fe concentrations in jacobsite, 2) Fe^{2+} distribution is dependent on the concentration of Fe^{2+} in rhodonite and 3) Mg distribution is dependent on the concentration of Mg in both the phases and also on the Mn^{2+}/Mg ratio in jacobsite. Most of these distribution coefficients also reveal distinct dependence on the grade of metamorphism.