

COEXISTING PHASES IN $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ SYSTEM WITH SPECIAL REFERENCE TO PYROPHYLLITE-DIASPORE DEPOSITS OF BUNDELKHAND COMPLEX

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The mineral assemblages of the pyrophyllite-diaspore deposits of the Bundelkhand Complex belong to the $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ system. They represent result of a very low grade metamorphism (below 350°C) of the quartz-aluminous deposits containing kaolinite, diaspore and quartz. Thermodynamic considerations of existing phases show that the minerals are in mutual equilibrium and water was a fixed component during metamorphism; and a hydrothermal origin of these deposits is therefore not supported.

INTRODUCTION

THE pyrophyllite-diaspore deposits are spread all over the Bundelkhand terrain of Central India. The associated rocks are granites, gneisses, phyllites, quartzites and dolerites which have been dated by Crawford (1970) about 2550 my., (Rb-Sr). Main contributions about these deposits are of Misra (1944, 1953), Misra and Sood (1947), Prakash, Singh and Saxena (1970), Singh *et al.*, (1976), and they all favour a hydrothermal origin. Contrary to these previous workers' assumptions, the present author is of the opinion that these deposits are a result of metamorphism of pre-existing clays containing kaolinite, gibbsite or diaspore, and quartz. The present work is a study of phase relationship of coexisting mineral phases in the light of experimental data available on the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$. On the basis of stability fields of different minerals, approximate temperature and pressure of their formation, i.e., grade of metamorphism has been assigned. Depending on the presence of hydrous and anhydrous phases it has been assumed that water was a fixed component and has played a major role in the genesis of these minerals at lower temperature.

Petrological aspect of these deposits has not been studied by the previous workers, therefore, the present work is an attempt to treat this problem in the light of thermodynamics of open (hydrothermal) and closed systems saturated with water. The coexisting mineral phases throw new light on the metamorphism of pyrophyllite-diaspore deposits which belong to the green schist facies metamorphism of the associated rocks of Palar formation (Sharma, *in press*).

GEOLOGICAL SETTING

Bundelkhand Complex of central India constitute four major rock units, namely Kuraicha formation, Palar formation, Bundelkhand granites and Bundelkhand dolerites. In between Kuraicha and Palar formations occur the pyrophyllite-diaspore deposits which show a stratigraphic control in their distribution. Their northeast trending outcrop pattern is a result of deformation in the area (Misra & Sharma, 1975).

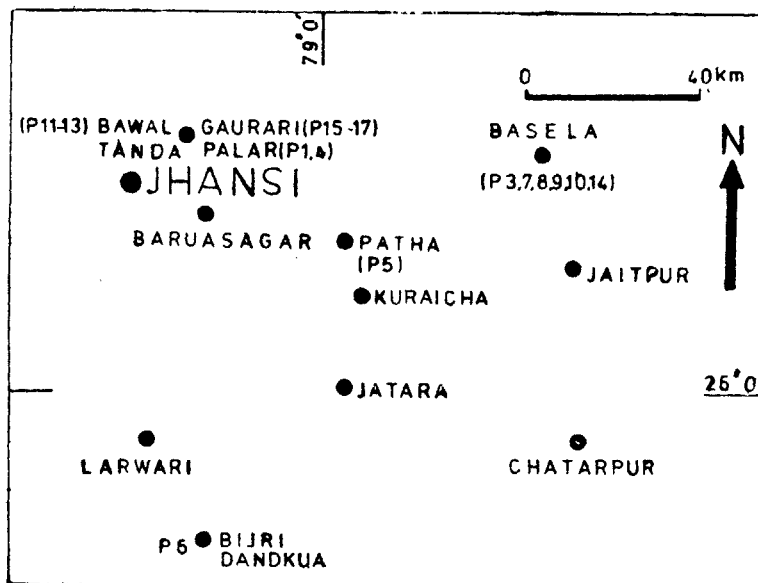


FIG. 1. Map showing location of samples and localities.

The rocks of the Palar formation with which these deposits are associated, are highly foliated and bear imprint of multiple deformation. Field observations suggest their syn- and post-mineralisation deformations which have manifestations on their outcrop pattern and localisation. Sixteen samples from these deposits, representing all types of mineral variations have been analysed and they are discussed in this paper (Fig. 1; Table I). Pyrophyllite, diaspore, kaolinite, muscovite, hematite and magnetite are the chief mineral constituents; however their mineral modes show a greater degree of variation from one locality to other and even in same locality.

STABILITY FIELDS OF SOME MINERAL PHASES

Major constituents of the pyrophyllite-diaspore deposits of Bundelkhand region are associated with kaolinite and muscovite. Their coexistence can be understood with the help of Al_2O_3 - SiO_2 - H_2O and K_2O - Al_2O_3 - SiO_2 - H_2O systems. Therefore, it is necessary to review the data about stability fields of different mineral phases of these systems.

The occurrence of pyrophyllite in very low grade metapelites (Winkler, 1974, p. 198; Frey, 1970; and Weber, 1972) sets on doubt the lower limit of pyrophyllite stability fields deduced in several experiments. Frey has suggested that kaolinite + 2 quartz \rightleftharpoons pyrophyllite + H_2O takes place at the beginning of metamorphism, i.e., at about 200 °C. The experimental work of Thompson (1970) shows that the pyrophyllite can be formed at 325 °C and 1 kb water pressure. Still lower temperature of 292 to 310 \pm 5 °C has been obtained in the kaolinite + 2 quartz \rightleftharpoons pyrophyllite + H_2O reaction carried out by Velde and Kornprobst (1969). In the light of the mineralogical composition of the Bundelkhand deposits, the following reactions are significant :

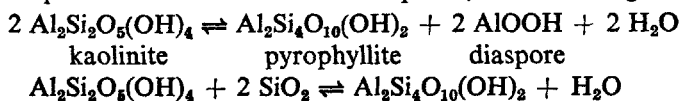


TABLE I

Major element analyses of the samples carried out by the atomic absorption and flame photometry in wt. % Fe as determined by XRF and shown as Fe_2O_3 , and locations of the samples shown on Fig. 1

Oxides	Samples:							
	P 5	P 3	P 7	P 8	P 9	P 10	P 14	P 6
TiO ₂	0.5	1.0	0.4	1.4	1.0	1.0	0.7	0.8
SiO ₂	8.9	64.7	62.8	58.4	55.9	58.8	65.7	—
Al ₂ O ₃	76.9	27.4	29.5	30.3	33.3	29.8	27.6	83.3
Fe ₂ O ₃	0.4	1.7	0.4	0.5	1.0	0.5	0.4	0.5
MnO	—	—	—	—	—	—	—	—
MgO	—	tr	tr	—	—	—	tr	—
CaO	—	—	—	—	—	—	—	—
Na ₂ O	0.1	—	0.1	0.1	—	—	—	—
K ₂ O	0.5	—	1.7	2.9	5.3	2.9	—	—
H ₂ O	13.6	4.9	4.7	4.7	4.4	4.8	4.9	14.4
Total	100.9	99.7	99.6	98.3	100.9	97.8	99.3	99.0

Oxides	Samples:							
	P 1	P 4	P 15	P 16	P 17	P 11	P 12	P 13
TiO ₂	0.5	0.5	2.9	0.5	3.3	0.4	0.5	0.4
SiO ₂	—	66.7	30.9	31.9	11.8	65.7	65.7	65.7
Al ₂ O ₃	85.0	28.3	55.2	56.9	63.1	28.8	28.6	28.8
Fe ₂ O ₃	0.24	0.8	2.1	0.7	11.4	0.7	0.8	0.8
MnO	—	—	—	—	—	—	—	—
MgO	—	—	—	—	—	tr	—	—
CaO	—	—	—	—	—	—	—	—
Na ₂ O	—	—	—	—	—	—	—	—
K ₂ O	—	—	—	—	—	tr	—	—
H ₂ O	15.0	5.0	9.9	10.6	11.4	5.4	5.6	5.4
Total	100.7	101.3	101.0	100.6	100.6	101.0	101.2	101.1

An upper stability limit of pyrophyllite has been determined by Hemley *et al.* (1967) and Kerrick (1968) as 400 ± 15 °C at 1 kb water pressure for the reaction



Allen (1952) and Kennedy (1959) are of the opinion that diaspore can form at atmospheric pressure and temperature. Kennedy has given a gibbsite break down curve (gibbsite \rightleftharpoons diaspore) between 100 and 200 °C, and diaspore break down at about 400 °C and lower pressure. This can be considered the field of diaspore at lower pressure. Further supporting these experimental results is the occurrence of diaspore in the lateritic profile over granite of Kot area in western India (Köster, 1961). The natural occurrences of pyrophyllite and diaspore in the very low temperature-pressure mineral assemblages suggest their genesis even at much lower P-T conditions than what is known from experimental results. Fig. 2 is a summary of the knowledge based on the published experimental data discussed in this paper about the stability fields of some important minerals and reactions. Boundaries of kyanite, andalusite

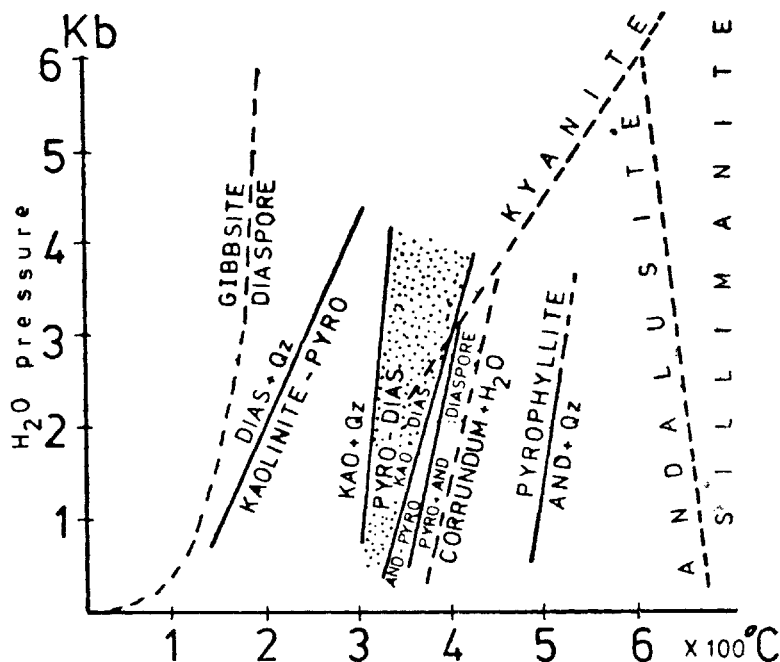


FIG. 2. P-T conditions of common reactions and stability fields of important minerals based on published experimental data referred to in the text. The stippled area shows the field of metamorphism of the pyrophyllite-diaspore deposits of the Bundelkhand Complex deduced in this work.

and sillimanite have been plotted from Richardson, Gilbert and Bell (1969) and Zen (1969).

$\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ SYSTEM

The chemical analyses of samples are given in Table I. They have been plotted on a three-component triangle which forms the $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ ternary system. All the samples can be represented in this diagram (Fig. 3) and are part of the system. The coexistence of mineral phases is clearly understandable in the thin section study. In the present mineralogical set-up kaolinite, pyrophyllite, diaspore and quartz may exist as stable phases. Except quartz, rest of the minerals are most prevalent in all the deposits of the Bundelkhand region. The set of samples analysed here may also be considered to belong to a four-component system due to the presence of K_2O in some of the samples. The maximum number of phases which can be represented by the ternary system are three in the samples P15, P16 and P17. The two samples P1 and P6 represent a two component system $\text{Al}_2\text{O}_3\text{-H}_2\text{O}$. The samples of Palar area, lie on the diaspore-pyrophyllite tie line. In the same area, the samples collected from Gaurari quarry lie in the triangular space of diaspore-pyrophyllite-kaolinite and are in ternary phase. In a thin section study, these three minerals show common mineral boundaries. They are in equilibrium while the system is univariant. It is comparable with the similar univariant system experimentally worked out by

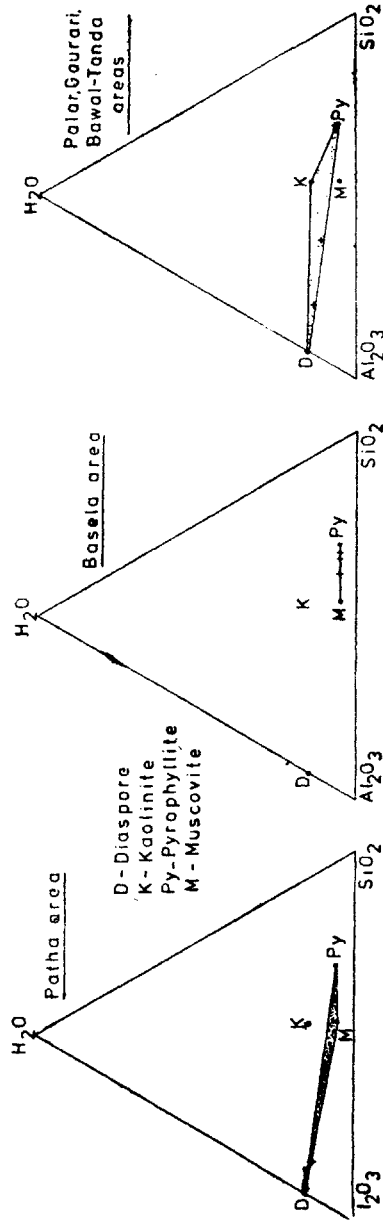


FIG. 3. The mineral phases of the Bundelkhand samples are plotted in the ternary system. Kaolinite (K), pyrophyllite (Py), muscovite (M) and diaspore (D) are the minerals in the system.

Velde and Kornprobst (1969). Their reaction curves 1 and 4 in their Fig. 2 provide such field of coexistence of these mineral phases. This information about experimental data indicate a temperature below 350 °C and lower pressure. Another locality of the Garhmau lake area is Bawal-Tanda where two phase assemblages are common. The samples from Patha and Basela areas belong to the $K_2O-Al_2O_3-SiO_2-H_2O$ system, but the phases of the ternary system are plotted in Fig. 3 omitting the four-component phase of muscovite. These samples contain diaspore and pyrophyllite and instead of kaolinite, muscovite is present. Muscovite is a consequence of K_2O in the system which is an independent variable. This is due to the difference in the physico-chemical condition in the two areas which is supported by the degree of freedom given in Table II for the phases present in different samples. The Basela samples show two phase assemblages. The tie lines kaolinite-quartz, pyrophyllite-quartz, and muscovite-kaolinite of this system do not exist in the Bundelkhand samples.

Because of the absence of anhydrous phases in these samples it is logical to assume that water may have existed as a phase in equilibrium at the time of pyrophyllite genesis. In connection with the pyrophyllite deposits of North Carolina, Zen (1961) has mentioned that with the system free of H_2O andalusite and quartz coexist while in the very hydrous system kaolinite and quartz coexist. Therefore, assuming a hydrous system for Bundelkhand samples the following phases are stable in nature :

- (a) diaspore-pyrophyllite-kaolinite- H_2O
- (b) diaspore-pyrophyllite-muscovite- H_2O
- (c) pyrophyllite-kaolinite- H_2O
- (d) pyrophyllite-muscovite- H_2O
- (e) pyrophyllite- H_2O
- (f) diaspore- H_2O

Of these mineral phases present in the samples only the three-phase assemblages (a and b) are of petrologic significance and can be used for the study of phase relationship. Though the phase relationship for six samples has been computed and given in Table II, only samples P15, P16, P17 and P5 indicate the thermodynamics of the system. Because other samples contain lesser number of phases which may be due to the sample bias, size of the phases and the size of the system. The phase relationship given in Table II shows that the system is in equilibrium. The degree of freedom has been computed for H_2O as an existing phase in equilibrium. The metamorphic systems are not closed in the strict sense. In the present case, these deposits were under the thick cover of quartzites and metapelites; it is assumed that the system was closed. Therefore, water was a fixed component during metamorphism. In such a closed system, the maximum number of phases 5 or 6 can be present in an invariant system i.e., $F = 0$; and the phases present in the Bundelkhand samples are less than this number therefore, chances of being in equilibrium are more. To satisfy conditions of phase rule of a closed system the degree of freedom are positive number in the assemblages listed in Table II. If H_2O is not an additional phase, the systems are divariant in the case of ternary system and trivariant in the case of four component system but in the case of water as an additional phase then the systems were univariant in 'ternary system' and divariant in 'four component system' as shown in Table II. In all the cases, the systems are in equilibrium. The

TABLE II

Phase relationship and degree of freedom computed for existing mineral phases

(Values in the bracket are maximum number of phases possible if $F=0$. F =degree of freedom; C = components; P =phases c' = mobile component; py = pyrophyllite; di = diaspore; k = kaolinite, m = muscovite)

Sample No. and mineral assemblage	$F = C - P + 2$ without H_2O phase	$F = C - P + 2$ H_2O as a phase	$\phi_{max} = C - c'$ Thompson (1955) Korzhinskii (1950)	Phases in natured samples with H_2O
P1 (di)	3 (4)	2	1	2
P15 (di/py/k)	2 (5)	1	2	4
P16 (di/py/k)	2 (5)	1	2	4
P17 (di/py/k)	2 (5)	1	2	4
P 5 (di/py/m)	3 (6)	2	3	4
P11 (py/k)	3 (5)	2	2	3

application of phase rule suggested by Turner (1968, p. 57) indicates that the phases in a system are in equilibrium at di- and uni-variant conditions. The petrographic phase relationship of the Bundelkhand deposits is consistent with this view. The rest of the samples which are not included in the Table II contain lesser number of mineral phases and show a higher number of variance which indicate influence of composition along with other physical parameters and heterogeneity of the primary composition. Distribution of primary components plays an important role in the distribution of final phases. This causes difference in the existing mineral phases in a sample and in the outcrop. Mobility of the components in a metamorphic process is very low so these variations are preserved in the final phases.

In the case of sample P1 the system is divariant when H_2O is a phase in equilibrium. It may be a result of gibbsite \rightleftharpoons diaspore transformation with a stable phase represented by a dependent/independent set of variables and composition. The sample P4 contains pyrophyllite and may have been in equilibrium with H_2O represent a trivariant system. In this case pressure, temperature and composition are the probable variables which restrict the other phases to exist. For pyrophyllite genesis, the reaction $kaolinite + 2 quartz \rightleftharpoons pyrophyllite + H_2O$, requires 1 : 2 ratio of kaolinite : quartz, therefore, composition is a variable in this case. Composition has played a major role in the distribution of different mineral phases.

The other aspect of thermodynamic consideration is of an open system. Thompson (1955) and Korzhinskii (1950) have shown that the maximum number of phases in an open system is related to the number of components and the number of mobile variables. In a ternary system Al_2O_3 - SiO_2 - H_2O , only two phases can coexist if the system is open as in hydrothermal solutions. Therefore, four phase assemblages occurring in the pyrophyllite-diaspore deposits of Bundelkhand region are thermodynamically not possible in a hydrothermal system and need to be explained.

METAMORPHISM

The pyrophyllite-diaspore deposits of the Bundelkhand Complex are highly foliated, faulted and sheared. Misra and Sharma (1974) have discussed their structure

and consider them to be intimately associated with the rocks of Palar formation and have been involved in folding. With the information about stability fields of important minerals (Fig. 2), it is possible to say that the metamorphic grade of these deposits has not crossed the upper stability limit of pyrophyllite field, i.e., 400 °C. In this regard, absence of anhydrous aluminium silicates is conspicuous. The system has been considered to be a very hydrous one. Fig. 2 shows that the stability field of andalusite is a narrow region within the pyrophyllite field. Zen (1961) has described that in a very hydrous system andalusite does not appear. Roy and Osborn (1954), and Clark *et al.* (1957) have shown that sillimanite and mullite occur in place of andalusite if the system is in equilibrium with pure H₂O. Thompson (1955) has shown that with the dilution of the fluid phase the breakdown curve of pyrophyllite shifts towards the lower temperature and enters the stability field of andalusite. This is a most probable condition of natural system, therefore the metamorphism of the pyrophyllite-diaspore deposits of the Bundelkhand region has not reached the limit where andalusite appears. This means that the temperature of metamorphism may have been below 350 °C.

It is assumed that the pre-metamorphic mineral assemblage contained kaolinite, gibbsite or diaspore, quartz, illite or muscovite. Metamorphism of these minerals can give rise to the Bundelkhand type mineral deposits. Kaolinite and muscovite rarely coexist but either of the two is common with diaspore and pyrophyllite. The samples analysed in this work are free of quartz and it seems that whatever quartz was present in the sediments has reacted with kaolinite to form pyrophyllite. Due to the shortage of quartz entire content of kaolinite could not react to form pyrophyllite, therefore, it coexists with other minerals. The samples from Basela contain 15 to 45 per cent muscovite but they are also associated with lumps of pure pyrophyllite. In this sequence it is very likely that some of K-feldspars may have been preserved in the premetamorphic assemblage and later have reacted to form muscovite. The other possibility is that along with kaolinite, illite may have been formed; the later during metamorphism may have changed into muscovite.

CONCLUSION

In the light of the above discussion of coexisting mineral phases and their thermodynamic considerations, it is clear that the pyrophyllite-diaspore deposits of the Bundelkhand region contains mineral assemblages of ternary system where H₂O is a fixed component. The system was a closed one. The absence of free quartz indicates that the system had no surplus silica for quartz to exist at least in the samples studied. This does not rule out a possibility that quartz may coexist as a phase. However, the absence of quartz further disapproves any hydrothermal influence (a mobile water component) because the latter is often rich in silica as compared with aluminium—a major component of these deposits. Had there been water as a mobile component then more than two phases would not have equilibrated thermodynamically. Thus more than two minerals would not have occurred. Therefore, the minerals like pyrophyllite, diaspore, kaolinite, and (quartz may also occur) found in coexistence cannot form from a hydrothermal solution. It should be mentioned here that the vein quartz and tectonic quartz bodies found in these deposits are secondary in origin and do not show coexisting phases. They are younger than

the pyrophyllite genesis. Absence of the kaolinite-quartz tie line in the phase diagrams supports the important reaction $kaolinite + 2 quartz \rightleftharpoons pyrophyllite + H_2O$.

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