

Structural parallels between the high-pressure B phases and the leucophoenicite series

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ABSTRACT

The high-pressure phases denoted ANH-B, hydrous B, and SHY-B (Finger et al., 1991; Pacalo and Parise, 1992), containing both ^{44}Si and ^{66}Si , are members of a homologous (polysomatic) series in which the ^{44}Si -containing portions are composed of olivine-like (O) slabs alternating with thinner goethite-like (G) slabs in the ordered arrangements O^∞ , OOOG , and OG . Leucophoenicite, OOOG , containing the same kind of slabs, represents the only macroscopic member of the leucophoenicite series (White and Hyde, 1983). It has the same slab sequence as the hydrous B phase; lamellar micromembers were found with O^{G} . The principal difference between the two series is that the leucophoenicite series lacks the purely octahedral layers with ^{66}Si that are intercalated with the ^{44}Si -containing ones in the B phases. These relationships allow one to predict further members for both series. They also suggest possible homologues that are intermediate between the two series, e.g., between leucophoenicite and hydrous B and between the hypothetical OG leucophoenicite and SHY-B, and contain a smaller proportion of ^{66}Si -based layers than these B phases. Mn might play a stabilizing role in the B series. Hypothetical B phases based on O slabs alternating with norbergite-like (N) slabs are much richer in Mg and have lower H_2O -storing capacity.

INTRODUCTION

In their structural description of the high-pressure phase referred to as anhydrous B, $\text{Mg}_{14}\text{Si}_5\text{O}_{24}$, Finger et al. (1991) described olivine-like double layers that alternate with purely octahedral layers containing ^{66}Si and vacancies in an ordered arrangement. They defined olivine and ANH-B as two homologues of a possible series with a variable layer ratio. The other, similarly intercalated high-pressure phase denoted hydrous B, $\text{Mg}_{12}\text{Si}_4\text{O}_{19}(\text{OH})_2$, has similar double layers containing ^{44}Si and was referred to by Finger et al. (1991) as loosely related to the humite series. Pacalo and Parise (1992) described the structure of superhydrous B, $\text{Mg}_{10}\text{Si}_3\text{O}_{14}(\text{OH})_4$, and related these three structures to one another by means of crystallographic shear.

Moore (1970) described the structure of leucophoenicite, $\text{Mn}_7\text{Si}_3\text{O}_{12}(\text{OH})_2$, as superficially similar to that of the humite series. White and Hyde (1983) described the relationship between leucophoenicite and the humite series, as well as the structure defects and inhomogeneities in leucophoenicite, in terms of cationic framework and crystallographic shear planes, coining the term leucophoenicite homologous series.

In studies of the structural relations among magnesium, manganese, and iron silicates, hitherto unrecognized structural parallels between the high-pressure B phases and the leucophoenicite series were found. The objective of the present work is to clarify the crystal chemistry of

the B phases, which may help in planning further syntheses based on the relationships recognized here.

THE LEUCOPHOENICITE SERIES

The leucophoenicite structure is composed of infinite zig-zag chains of coordination octahedra and is superficially similar to the humite series. In the humite homologues, the straight chain segments have either one additional octahedron intermediate to those at the chain breakpoints (defining olivine-like slabs, O, in the polysomatic description of Thompson, 1978) or two octahedra in this interval (norbergite-like slabs, N, with OH groups) (Fig. 1). Only two types of segments are present in the known macroscopic phases; they are ordered in different proportions: O^∞ (olivine), NOOO (clinohumite), NOO (humite), NO (chondrodite), and N^∞ (norbergite) (Thompson, 1978). Counting the intermediate octahedra in individual segments, this series can be expressed as 111, 2111, 211, 21, and 222; counting the total number of octahedra in straight strip segments, this series represents combinations 222, 3222, 322, 32, and 333, conforming with the notation of White and Hyde (1983).

In leucophoenicite, the longer segments of zig-zag chains contain only one octahedron intermediate to those on the breakpoints, as indicated in Figure 2. These chains are the O layers defined above. The shorter segments have no intermediate octahedra and have a goethite-like or groutite-like $[\alpha\text{-MnO}(\text{OH})]$ structure. The relevant slabs,

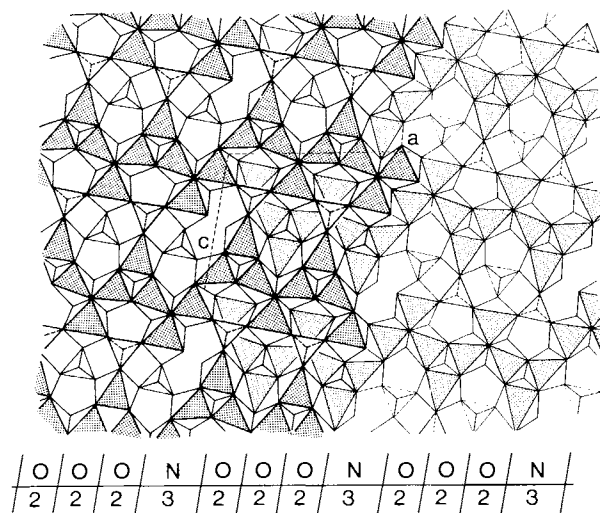


Fig. 1. The crystal structure of clinohumite (Robinson et al., 1973) projected along [010]. The two layers, $\frac{1}{2}b$ apart, are indicated in the left and right portions of the figure, and a complete structure is shown in the central portion. Polysomatic slabs are indicated by O and N notation as well as by the number of octahedra (2 and 3).

G, are a half-octahedron thick. SiO_4 tetrahedra attached to the apical octahedra in the O slabs have full occupancy, whereas those straddling the O-G boundaries have half occupancy, alternating on a statistical basis with OH groups (Fig. 2; Moore, 1970; White and Hyde, 1983).

Leucophoenicite is an ordered structure: OOOG, i.e., 01^3 , counting intermediate octahedra, and 12^3 (White and Hyde, 1983) counting all octahedra in individual slabs. White and Hyde (1983) also found O^4G , O^5G , and O^6G as slab-like micro-domains, often yielding considerable disorder or quasi-periodic, long-range repetition in the structure. If one generalizes the leucophoenicite series (O^nG or 12^n) to lower n values, the most prominent simple member will be OG, or 1212, in terms of the number of octahedral strings per slab. This phase has not yet been found in nature. The general chemical formula of the leucophoenicite series is $\text{Mn}_{2n+1}\text{Si}_n\text{O}_{4n}(\text{OH})_2$, derived from the composition of olivine and leucophoenicite as the two available members. The coefficient n is equal to the number of O slabs between two consecutive G slabs. For the G^∞ end-member, the formula $\text{Mn}(\text{OH})_2$ results. The general chemical formula of the humite series, on the basis of the number n of O slabs between two consecutive N slabs, is $\text{Mg}_{2n+3}\text{Si}_{n+1}\text{O}_{4n+4}(\text{OH})_2$.

In compositional space (Mg, Mn)O-SiO₂-H₂O, both series are of limited extent because each combines slabs with only two thicknesses and compositions. The leucophoenicite series shares one set of slabs (O) with the humite series. Therefore, in a polyhedral description, these two series can be treated as special cases of a series of structures having one, two, three, or more octahedral strings in the straight segments between two consecutive chain breakpoints [slab types 1, 2, 3, 4, ... in White and

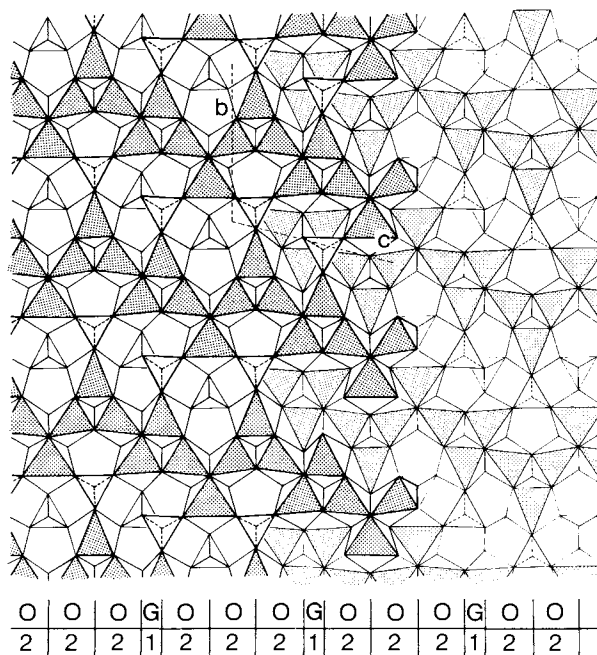


Fig. 2. The crystal structure of leucophoenicite (Moore, 1970) projected along [100]. The two layers, $\frac{1}{2}a$ apart, are indicated in the left and right portions of the figure, and a complete structure is shown in the central portion. Polysomatic slabs are indicated by O and G notation as well as by the number of octahedra (1 and 2).

Hyde's (1983) notation]. Experience shows (White and Hyde, 1982a, 1982b, 1983) that the known portion of this infinite series is combinatorial in the 1-2 and 2-3 intervals (the two polysomatic series described above), and that, except for rare structural errors, these two intervals are separate.

THE SERIES OF HIGH-PRESSURE B PHASES

The double layers with ^{44}Si in the structures of the B phases have zig-zag chains that are configurational equivalents of those in the leucophoenicite series [but are different in configuration from those in the humite series, as already observed by Finger et al. (1991) for the hydrous phase B]. The ANH-B double layer (Finger et al., 1991) corresponds to the OOO (i.e., 2^∞) sequence, the hydrous B double layer corresponds in detail to the leucophoenicite sequence OOOG ($=12^3$), and the SHY-B double layer corresponds to the hypothetical leucophoenicite homologue OGOG ($=12$) (Fig. 3). Vacancies and ^{16}Si sites in the intercalated octahedral layers follow a pattern dictated by the leucophoenicite-olivine double layers: orthohexagonal in SHY-B, rectangular in ANH-B, and a composite of these in hydrous B.

Significantly, the analogy between the leucophoenicite phases and the B phases extends to the placement of OH groups and statistical Si tetrahedra on O-G boundaries. In leucophoenicite, Si tetrahedra and OH groups occur randomly in the two available adjacent sites (Moore, 1970;

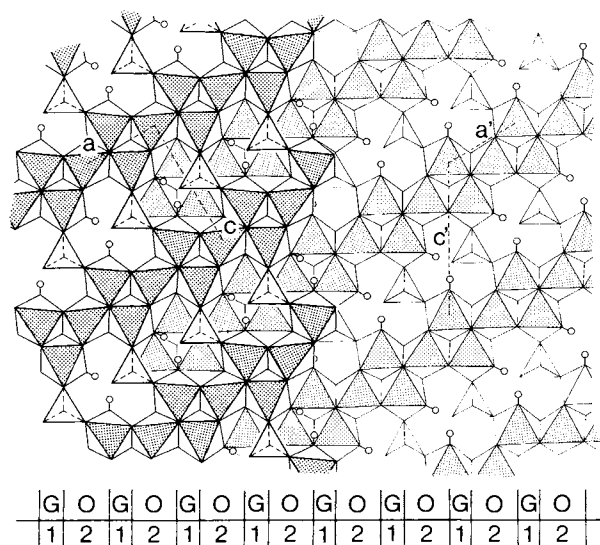


Fig. 3. The ^{16}Si -based double layer from the crystal structure of SHY-B (Pacalo and Parise, 1992) projected along $[010]$. Primed symbols indicate an alternative, leucophoenicite-compatible monoclinic cell. H positions are indicated by circles; other details as in Fig. 2.

White and Hyde, 1983); in the B phases they are fully ordered (Finger et al., 1991; Pacalo and Parise, 1992), and the O-H...O bonds occur within the leucophoenicite-like double layer. The formula of the B series, with the ratio of ^{14}Si - to ^{16}Si -containing layers equal to 2:1, is $\text{Mg}_{7n+3}\text{Si}_{2.5n+0.5}\text{O}_{12n+2}(\text{OH})_4$. It is based on the extrapolated composition of O slabs, $\text{Mg}_7\text{Si}_{2.5}\text{O}_{12}$, and G slabs, $\text{Mg}_3\text{Si}_{0.5}\text{O}_2(\text{OH})_4$.

DISCUSSION AND GENERALIZATIONS

Comparison of the leucophoenicite series with the series of high-pressure B phases (Table 1) suggests that there exist homologous pairs: olivine-anhydrous B, leucophoenicite-hydrous B, and the hypothetical (2,1) \equiv OG phase-superhydrous B. Each series could be a basis for a combinatorial (polysomatic) series of homologues in which the ratio of ^{14}Si - to ^{16}Si -based layers progressively decreases (compare also Finger and Hazen, 1991). Thus, each phase belongs to two homologous series along two

different directions of compositional space. The homologous (polysomatic) changes prescribed by these two series act on distinct sets of slabs in the structure of this phase; these slabs are oriented perpendicular to each other. Potentially, the different ^{16}Si - ^{14}Si layer ratios might reflect different pressure conditions.

Leucophoenicite and its partly disordered forms are manganese silicates with only minor amounts of Ca, Mg, and Fe. Introduction of Mn into B phases might stabilize them at lower pressures and allow the existence of homologues (polysomes) with a lower percentage of ^{16}Si -containing layers. On the other hand, the role of Mn might be limited to the partly substituted compositions such as $\text{Mn}_2\text{Mg}_{12}\text{Si}_5\text{O}_{24}$ for the B phase. Mn would partake in cation size balancing between ^{16}Si and M^{2+} (Hazen et al., 1992).

Ordering of OH groups and Si tetrahedra in the G slabs (and the immediately adjacent positions) of the structures of the hydrous B and SHY-B phases is determined by the need to maintain the orthohexagonal motif of Si octahedra and octahedral vacancies in the ^{16}Si -based layers. This motif yields the closest packing of clusters composed of 12 Mg octahedra surrounding an Si octahedron while still preserving the charge balance of the ^{16}Si -based layer. These clusters are fundamental structural features of high-pressure B phases (Finger and Hazen, 1991).

Rings of six Mg octahedra around octahedral vacancies of ^{16}Si -based layers have dimensions in the G portions larger than those of similar Mg_6 rings around Si octahedra. OH groups occupy empty tetrahedra above and below these expanded ring portions. The Si tetrahedra immediately adjacent to the OH-occupied tetrahedra cap the octahedral vacancies from both sides.

It is these two adjacent Si- and OH-occupied tetrahedra that are found to be randomly interchangeable in the structure of leucophoenicite, which lacks ^{16}Si -based layers. Local charge balance and geometric requirements are bound to induce ordering even in leucophoenicite. However, along the $[001]$ direction ordering is subject to frequent errors because the ordering mechanism operates across recurring packs of three consecutive O slabs (Fig. 2). For leucophoenicite homologues with a lower proportion of O slabs (i.e., O^2G and OG) ordering is expected to be more pronounced.

TABLE 1. Structural information for the high-pressure B phases, olivine, and leucophoenicite

Phase	Composition	Space group	Lattice periods (Å) referring to			Reference
			Slab stacking	Stacking of oct-tet layers	Intraslab period	
ANH-B	$\text{Mg}_{14}\text{Si}_5\text{O}_{24}$	<i>Pmcb</i>	<i>a</i> 5.868(1)	<i>b</i> 14.178(1)	<i>c</i> 10.048(1)	Finger et al., 1991
Hydrous B	$\text{Mg}_{12}\text{Si}_4\text{O}_{19}(\text{OH})_2$	<i>P2₁/c</i>	<i>a</i> 10.588(2)	<i>b</i> 14.097(1)	<i>c</i> 10.073(1)	Finger et al., 1991
			<i>d</i> ₁₀₀ 10.269		β 104.10(3)	
SHY-B*	$\text{Mg}_{10}\text{Si}_3\text{O}_{14}(\text{OH})_4$	<i>Pnnm</i>	<i>a'</i> 5.089(1)	<i>b</i> 13.968(7)	<i>c'</i> 10.076(1)	Pacalo and Parise, 1992
			<i>d</i> ₁₀₀ 4.392		β 120.34(1)	
			<i>c</i> 5.981(1)		<i>b</i> 10.197(1)	
Forsterite	Mg_2SiO_4	<i>Pbnm</i>	<i>c</i> 11.324(9)	<i>a</i> 4.754(1)	<i>b</i> 10.197(1)	Ribbe, 1982
Leucophoenicite	$\text{Mn}_7\text{Si}_3\text{O}_{12}(\text{OH})_2$	<i>P2₁/b</i>	<i>a</i> 4.826(6)	<i>b</i> 10.842(19)	<i>b</i> 10.842(19)	Moore, 1970
			<i>d</i> ₀₀₁ 10.991		α 103.67(6)	

* Primed axes were recalculated to match those in other phases.

Leucophoenicite, OOOG ($n = 3$), is dimorphous with manganhumite, OON ($n = 2$), as also suggested by the formal equivalence $N \rightarrow O + G$. The unit-cell volume of leucophoenicite, recalculated to a pure Mg composition using the forsterite and tephroite unit-cell volume ratio (data tabulated by Ribbe, 1982), is 521 \AA^3 ; that of hydroxyl-humite is 513 \AA^3 , whereas one-third of the unit-cell volume of B at ambient pressure is 511 \AA^3 . Within the limits of error, these volumes are identical. Therefore, the reasons why the B phases adopt the leucophoenicite and not the humite motif must be more subtle than a mere volume difference.

Simulated B phases with O and N slabs (instead of O and G slabs) have the general formula $\text{Mg}_{12+7n}\text{Si}_{2.5(1+n)}\text{O}_{4(4+3n)}(\text{OH})_2$, where n is the number of O slabs between two consecutive N slabs. These B phases are based on mixing O slabs, $\text{Mg}_7\text{Si}_{2.5}\text{O}_{12}$, with hypothetical N slabs, $\text{Mg}_{12}\text{Si}_{2.5}\text{O}_{16}(\text{OH})_2$. The latter slabs were derived by preserving both the clusters of 12 Mg octahedra around ^{60}Si positions and the rings of six Mg octahedra plus two capping Si tetrahedra around octahedral vacancies.

The B phase that is homologous to norbergite (N^∞) should have the composition $\text{Mg}_{12}\text{Si}_{2.5}\text{O}_{16}(\text{OH})_2$. Following the above used analogy $N \rightarrow O + G$, this B phase should be a dimorph of the $(\text{OG})^\infty$ phase SHY-B. However, this is not the case. Although norbergite (N^∞) and leucophoenicite $(\text{OG})^\infty$ are dimorphs of $\text{Mg}_3\text{SiO}_4(\text{OH})_2$, the corresponding B phases differ in composition. The norbergite-based, hypothetical B phases are much richer in Mg and have lower H_2O -storing capacity than the corresponding leucophoenicite-based B phases observed in high-pressure experiments. The ^{60}Si -based layers in the N slabs can be derived from the corresponding slabs in SHY-B by intercalation of an additional (001) slab of Mg octahedra.

For the ^{60}Si -based layers, the trend from ANH-B toward hydrated O-N phases is in a direction opposite to that observed for O-G phases. In the O-N phases the Mg-Si ratio increases and Mg octahedra are unshared or shared

by two Mg clusters. In the O-G phases, the Mg-Si ratio decreases, and sharing of octahedra by Mg clusters increases from two to three clusters for each octahedron. If the small Si octahedra can still be accommodated in Mg-rich O-N octahedral layers, the norbergite-based series of B phases should occur in Mg-rich environments.

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