Ribbeite, a second example of edge-sharing silicate tetrahedra in the leucophoenicite group

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ABSTRACT

Ribbeite, $Mn_5(OH)_2(SiO_4)_2$, is orthorhombic *Pnma* with $a = 10.732(1)$ Å, $b = 15.672(6)$ Å, $c = 4.811(1)$ Å, $Z = 4$, and $V = 809.2$ Å^3. Its structure has been determined by direct methods and refined to a residual of 0.037 (unweighted) for all reflections. Ribbeite is structurally related to leucophoenicite in that it contains serrated, edge-sharing chains of Mn octahedra and two distinct types of Si tetrahedral sites: (1) a single, isolated, fully occupied Si tetrahedron, and (2) a pair of edge-sharing, half-occupied Si tetrahedra, which are related by an inversion center. Ribbeite is the unit-cell-twinned dimorph of alleghany-ite; the disordered edge-sharing tetrahedra in ribbeite are a direct consequence of mixed unit-cell glide operations in alleghanyite: statistically, half of the glides are alternate, half are *en echelon*. The valence requirements of O atoms in edge-sharing tetrahedra are met by two H bonds and one anomalously short Si-O distance of 1.522(3) Å.

INTRODUCTION

The new mineral ribbeite, $Mn_5(OH)_2(SiO_4)_2$, was described from the Kombat mine in Namibia by Peacor et al. (1987). They noted that it is orthorhombic, space group *Pbnm* or *Pbn2₁* (nonstandard settings), with lattice parameters $a = 4.799(1)$, $b = 10.742(6)$, $c = 15.70(1)$ Å (obtained by least-squares refinement of the powder diffraction data), $Z = 4$, and with the calculated chemical formula $(Mn_{4.30}Mg_{0.60}Fe_{0.02}Ca_{0.02})_{4.94}Si_{1.90}H_{2.54}O_{10}$ (from electron microprobe analysis). In addition, Peacor et al. (1987) observed that ribbeite and alleghanyite are polymorphically related, with ribbeite belonging to the leucophoenicite group and alleghanyite to the humite group (Table 1).

The structures of the humite-group minerals are well known and have been reviewed by Ribbe (1982). They were originally described as periodic layers of olivine and brucite-sellaite (Taylor and West, 1928), but Ribbe et al. (1968) showed that this layer concept for humite structures is inappropriate. Thompson (1978) suggested a description with alternating modules of olivine and norbergite. White and Hyde (1982a, 1982b) described humites in terms of anion-stuffed cation arrays that correspond to those in either well-known alloy types or lamellar intergrowths of such alloys. The arrays can be described as twinned cubic-closest-packed (ccp) bands of octahedrally coordinated cations. Using this system, White and Hyde (1983a) described forsterite as twinned ccp $Mg(2)^2$, where the twin bands of Mg cations are two atoms wide and the superscript denotes the number of twin individuals (bands) in a unit cell. Norbergite is twinned

ccp $Mg(3)^2$, i.e., the unit cell is based on two twin bands that are each three atoms wide. Other members of the humite group are based on intergrowths of twin bands that are two and three atoms wide. The twin-layer repeat notation is given in Table 1. White and Hyde (1983a) noted that the older method of denoting humites, $nMg_2SiO_4 \cdot Mg(OH,F)_2$, corresponds to twinned ccp $Mg(3,2^x)$ with $n = x + 1$.

The relationship between leucophoenicites and humites was enigmatic (Dunn, 1985) until White and Hyde (1983a) noted that leucophoenicites $(1,2^x)$ are regular intergrowths of a twin band one atom wide with bands two atoms wide; the bridging structure common to $(3,2^x)$ humites and $(1,2^x)$ leucophoenicites is (2) olivine. White and Hyde (1983a) also observed that subjecting the olivine structure to repeated crystallographic shear produces successive members of the leucophoenicite group. Kato et al. (1989) noted that the twin operation is a glide plane, and Yau and Peacor (1986) generalized the relationship, stating that "a similar glide in every member of the humite family $(3,2^x)$ results in a structure of the leucophoenicite family $(1,2^{x+1})$." Table 1 summarizes the relationships between leucophoenicites and humites.

The structures of leucophoenicite (Moore, 1970) and jerrygibbsite (Kato et al., 1989) have been discussed in terms of unit-cell twinning by Yau and Peacor (1986). We now report the crystal structure of ribbeite, which is indeed the unit-cell-twinned dimorph of alleghanyite, as predicted by Peacor et al. (1987). Ribbeite is similar to leucophoenicite in that it contains two distinct types of tetrahedral sites: (1) a single, isolated, fully occupied Si tetrahedron, and (2) a pair of edge-sharing, half-occupied

TABLE 1. Summary of structure data for the humite and leucophoenicite groups

Mineral	Ideal formula	$nM_2^{2+}SiO_4 \cdot M^{2+} \cdot$ $(OH,F)_2$	Space group*	Twin formula**	Reference
Humite group					
Norbergite	$Mg_3(SiO_4)(OH)_2$	$n = 1$	$Pbnm$	$(3)^2$	Gibbs and Ribbe (1969)
MAN†	$Mn_3(SiO_4)(OH)_2$	$n = 1$	$Pbnm$	$(3)^2$	Francis and Ribbe (1978)
Chondrodite	$Mg_5(SiO_4)_2(OH)_2$	$n = 2$	$P2_1/b$	$(3, 2)$	Gibbs et al. (1970)
Alleghanyite	$Mn_5(SiO_4)_2(OH)_2$	$n = 2$	$P2_1/b$	$(3, 2)$	Rentzeperis (1970)
Humite	$Mg_7(SiO_4)_3(OH)_2$	$n = 3$	$Pbnm$	$(3, 2^2)^2$	Ribbe and Gibbs (1971)
Manganhumite	$Mn_7(SiO_4)_3(OH)_2$	$n = 3$	$Pbnm$	$(3, 2^2)^2$	Francis and Ribbe (1978)
Clinohumite	$Mg_9(SiO_4)_4(OH)_2$	$n = 4$	$P2_1/b$	$(3, 2^3)$	Robinson et al. (1973)
Sonolite	$Mn_9(SiO_4)_4(OH)_2$	$n = 4$	$P2_1/b$	$(3, 2^3)$	Kato et al. (1989)
Olivine group					
Forsterite	$Mg_2(SiO_4)$	$n = \infty$	$Pbnm$	$(2)^2$	Francis and Ribbe (1980)
Tephroite	$Mn_2(SiO_4)$	$n = \infty$	$Pbnm$	$(2)^2$	Francis and Ribbe (1980)
Leucophoenicite group					
Unknown	$Mn_3(SiO_4)(OH)_2$	$n = 1$		$(1, 2)?$	
Ribbeite	$Mn_5(SiO_4)_2(OH)_2$	$n = 2$	$Pbnm$	$(1, 2^2)^2$	this study
Leucophoenicite	$Mn_7(SiO_4)_3(OH)_2$	$n = 3$	$P2_1/b$	$(1, 2^3)$	Moore (1970)
Jerrygibbsite	$Mn_9(SiO_4)_4(OH)_2$	$n = 4$	$Pbnm$	$(1, 2^4)^2$	Kato et al. (1989)

* Conventional but nonstandard settings.
** After White and Hyde (1982a, 1982b, 1983a).
† Synthetic Mn analogue of norbergite.

Si tetrahedra, related by an inversion center. A transmission electron microscopy (TEM) study of leucophoenicite (White and Hyde, 1983b) supported the structure proposed by Moore (1970).

STRUCTURE SOLUTION AND REFINEMENT

Intensity measurements were made using an anhedral crystal of approximate dimensions $0.12 \times 0.16 \times 0.31$ mm; this crystal was selected from the type material of ribbeite (Peacor et al., 1987; Smithsonian Institution catalog no. NMNH 163208). Intensities of 1131 reflections with $\sin \theta \leq 0.818$ and constituting one asymmetric unit were measured with monochromatized $MoK\alpha$ radiation by an Enraf-Nonius CAD4 kappa-axis diffractometer, controlled by a MicroVAX 3100 computer. All calculations involved in the solution and refinement of the structure were performed using the Enraf-Nonius crystallographic software system MolEN. The intensities of six standard reflections were monitored during data measurement, and these showed a total average intensity change of 0.85%. Cell parameters were obtained by least-squares analysis using the setting angles of 24 reflections in the range $5° < \theta < 12°$. In the $Pnma$ standard setting, ribbeite is orthorhombic, with $a = 10.732(1)$ Å, $b = 15.672(6)$ Å, $c = 4.811(1)$ Å, $Z = 4$, and $V = 809.2$ Å³. Intensities were reduced to structure factor amplitudes by correction for Lorentz-polarization effects and application of an empirical absorption correction derived from ψ-scans of six reflections.

Peacor et al. (1987) determined that ribbeite has space group $Pbnm$ or $Pbn2_1$ ($Pnma$ or $Pna2_1$ in the standard settings). Intensity statistics were inconclusive for selecting either the centric or acentric structure. The noncentrosymmetric space group $Pna2_1$ was therefore arbitrarily chosen as the basis for structure solution by direct methods, using the Multan 11/82 package incorporated in MolEN. The first E map revealed the locations of Mn,

Si, and most of the O atoms; syntheses of electron density and difference electron density revealed the positions of the remaining atoms other than H. Least-squares structure refinement was performed using the 802 reflections having $I_{obs} > 3\sigma(I_{obs})$, where σ is the standard deviation from the counting statistics. The function minimized was $\Sigma w(|F|_{obs} - |F|_{cal})^2$, where $w = 4|F|_{obs}^2/\sigma^2(|F|_{obs}^2)$. With isotropic displacement factors, the refinement converged to a value of 0.059 for the unweighted residual. However, strong parameter interaction between pairs of nonequivalent atoms and the inability to refine all O atoms with anisotropic displacement factors suggested that the acentric structure was incorrect. Therefore, the centrosymmetric space group $Pnma$ was selected, and after appropriate reindexing of reflections, direct methods were again employed. An E map revealed the locations of Mn, Si, and all O atoms. Least-squares refinement of this structure with isotropic displacement factors converged to an unweighted residual of 0.069. A refinement of the total occupancy factor of Si2 yielded a value of 0.485(5). This corresponds to 3.88(4) atoms, which is equal to four atoms within three estimated standard deviations; i.e., the Si2 site is essentially 50% occupied.

Introduction of anisotropic displacement factors for all atoms reduced the residual to 0.032. At this point an inspection of the list of observed and calculated structure factors revealed a pattern of intense, low-angle reflections having $|F|_{obs} < |F|_{cal}$. A combined isotropic extinction correction (i.e., combining the effects of primary and secondary extinction) of the form $|F|_{obs}$ (corr.) $= |F|_{obs}[1 + g(|I|_{obs})]$ was therefore applied, and that further reduced the residual to 0.027. A difference synthesis revealed two small peaks of 0.5 e/Å³ situated at distances of 0.6 and 0.8 Å from the hydroxyl O atoms O5 and O6, respectively. These were assumed to be H atoms and were labeled H1 and H2, respectively. It proved possible to obtain reasonable bond parameters for H1 but not for H2,

TABLE 2. Positional (decimal fractions) and displacement (Å²) parameters in ribbeite

	x	y	z	B_{eq}
Mn1 8d	86850(5)	14501(3)	49334(9)	1.11(1)
Mn2 4c	59124(6)	¼	51449(14)	1.11(1)
Mn3 8d	64402(5)	06127(3)	−00408(10)	1.24(1)
Si1 4c	7779(1)	¼	0712(2)	0.55(2)
Si2 8d	4613(1)	0448(1)	5835(3)	0.65(3)
O1 8d	4616(2)	0432(1)	2672(5)	1.22(4)
O2 4c	7778(3)	¼	7381(6)	0.73(5)
O3 4c	9179(2)	¼	2125(6)	0.78(5)
O4 8d	7101(2)	1681(1)	2123(4)	0.75(3)
O5 8d	5286(2)	1373(1)	7311(5)	1.58(4)
O6 8d	3109(2)	0439(1)	7344(5)	1.37(4)
H1 8d	555(8)	126(5)	569(16)	1.7(17)
H2 8d	345	034	600	2.0

Note: Values in parentheses are estimated standard deviations. Si2, H1, and H2 sites are 50% vacant. Displacement factor for H1 was refined isotropically; that for H2 was arbitrarily fixed. No estimated standard deviations are shown for H2 because its coordinates were fixed at those taken from the difference synthesis.

and accordingly the coordinates of H2 were fixed at those taken from the difference map, whereas the displacement factor for H2 was arbitrarily fixed at 2.0 Å². The difference synthesis showed no evidence of atom splitting affecting the disordered atom Si2 or its coordinating anions.

The final values of the residual are 0.027 (unweighted) and 0.050 (weighted) for the 802 observed reflections and 0.037 (unweighted) for all 1131 reflections. Table 2 con-

tains the final positional and displacement parameters, Table 3[1] the observed and calculated structure factors, Table 4 selected interatomic distances and angles, and Table 5 the empirical bond valences calculated from the observed distances and the constants given by Brese and O'Keeffe (1991).

STRUCTURE DESCRIPTION AND DISCUSSION

The ribbeite structure (Fig. 1) consists of sheets of hexagonal close-packed O atoms at levels of approximately $z = 0.25$ and 0.75. Cation sites are located at levels of approximately $z = 0.00$ and 0.50. Mn octahedra form serrated edge-sharing chains that trend roughly parallel to b. Moore (1970) described the leucophoenicite structure in terms of a cluster of five edge-sharing MnO_6 octahedra; this cluster is also found in ribbeite (Fig. 1). Viewed as an anion-stuffed cation array (White and Hyde, 1982a, 1982b, 1983a), ribbeite has the twinned ccp $Mn(1,2^2)^2$ arrangement.

Ribbeite is also similar to leucophoenicite in that it contains two distinct types of tetrahedral sites: (1) a single, isolated, fully occupied Si tetrahedron and (2) a pair of edge-sharing, half-occupied Si tetrahedra related by an

TABLE 4. Selected interatomic distances (Å) and angles (°) in ribbeite

MnO₆ octahedra						
Mn1–O1	2.262(2)	Mn2–O2	2.273(3)	Mn3–O1	2.360(2)
O2	2.245(2)	O3	2.157(3)	O1	2.369(2)
O3	2.194(2)	O4	2.321(2) × 2	O4	2.095(2)
O4	2.202(2)	O5	2.158(2) × 2	O5	2.140(2)
O5	2.174(2)	MEAN	2.231	O6	2.123(2)
O6	2.146(2)			O6	2.153(2)
MEAN	2.204			MEAN	2.207
SiO₄ tetrahedra						
Si1–O2	1.603(3)	O2–O4	2.717(3) × 2	O4–Si1–O3	103.7(1) × 2
O3	1.649(3)	O2–O3	2.733(4)	O4–Si1–O2	114.7(1) × 2
O4	1.624(2) × 2	O3–O4	2.573(3) × 2	O4–Si1–O4	104.4(2)
MEAN	1.625	O4–O4	2.566(4)	O3–Si1–O2	114.4(2)
		MEAN	2.646	MEAN	109.3
Si2–O1	1.522(3)	O1–O1'	2.744(5)	O1–Si2–O1'	113.2(1)
O1'	1.761(3)	O1–O5	2.770(3)	O1–Si2–O5	114.5(1)
O5	1.769(3)	O1–O6	2.770(3)	O1–Si2–O6	114.4(1)
O6	1.770(3)	O1'–O5	2.831(3)	O1'–Si2–O5	106.6(1)
MEAN	1.706	O1'–O6	2.798(3)	O1'–Si2–O6	104.8(1)
		O5–O6	2.757(3)	O5–Si2–O6	102.3(1)
		MEAN	2.778	MEAN	109.3
H-O in edge-sharing tetrahedra						
H1–O5	0.85(8)	O5–H1···O1	126(7)		
O1	2.19(8)	O5–H1–O1'	85(5)		
O1'	2.77(8)	O5–H1–O6	64(5)		
O6	3.02(8)	O5–H1–O6'	135(6)		
O6'	3.36(8)				
H2–O6	0.76	O6–H2···O1	161		
O1	2.04	O6–H2–O1'	107		
O1'	2.48	O6–H2–O5	91		
O5	2.63	O6–H2–O5'	139		
O5'	3.40				

Note: No estimated standard deviations are given for distances or angles involving H2 because the position of this atom was fixed at the coordinates from the difference synthesis during the refinement.

TABLE 5. Empirical bond valences (vu) for ribbeite

	Mn1	Mn2	Mn3	Si1	Si2	Σv_a
O1	0.28		0.21 (×2)		(0.35*, 0.66*) → (0.70, 1.32) ↓	1.71
O2	0.29 (×2) → 0.29 ↓	0.27		1.06		1.91
O3	0.34 (×2) → 0.34 ↓	0.37		0.94		1.99
O4	0.33	0.24 → 0.24 (×2) ↓	0.44	1.00 → 1.00 (×2) ↓		2.01
O5	0.35	0.37 → 0.37 (×2) ↓	0.39		0.34* → 0.68 ↓	1.45
O6	0.38		0.37, 0.41		0.34* → 0.68 ↓	1.50
Σv_c	1.97	1.86	2.03	4.00	3.38	

Note: Valences for O-Si2 bonds marked with asterisks are given as 50% of their calculated values to account for the 50% occupancy of the Si2 site.

inversion center. As noted by Moore (1970), the absence of Si in one of the edge-sharing tetrahedral pairs implies that (OH)⁻ has replaced O²⁻. Thus, when Si2(0.58) (Fig. 2) is absent, H1(0.57) and H2(0.60) are present, forming OH groups with O5(0.73) and O6(0.73), respectively. However, the valence requirements of O1(0.27) are also unsatisfied in the absence of Si2(0.58) and can only be met by the formation of H bonds from H1(0.57) and H2(0.60). This is supported by short H-O1 distances (Table 4) of 2.19(8) Å for H1(0.57)–O1(0.27) and 2.04 Å for H2(0.60)–O1(0.27). Additional support comes from the empirical sums of bond valence (Table 5): the sum for O1 is conspicuously low at 1.71 vu, whereas the sums for the other nonhydroxyl O atoms O2, O3, and O4 are all within 0.10 vu of their ideal values.

Valence requirements of O1'(0.73) (Fig. 2) are likewise unsatisfied in the absence of Si2(0.58), since this Si atom is coordinated to both O1 and O1', which form the shared

edge of the tetrahedral pair. However, in this case the valence requirements of O1'(0.73) cannot be satisfied by the formation of H bonds because bond distances (Table 4) are too long: 2.77 Å for H1–O1', and 2.48 Å for H2–O1'. Baur (1972) notes that "only H · · · O distances shorter than 2.4 Å should be considered to be hydrogen bonds." Instead, the distance Si2(0.42)–O1'(0.73) in the occupied Si2 tetrahedron contracts to a very short 1.522 Å to satisfy the valence needs of O1'(0.73).

When Si2(0.58) (Fig. 2) is absent, Si2(0.42) must be present. This fulfills the valence requirements of its associated O5' and O6' ligands, and the latter are therefore oxide rather than hydroxyl O atoms. Atoms H1(0.43) and H2(0.40) must be absent, and the occupancies of H1 and H2 are therefore correlated with the occupancy of Si2, i.e., at 50% in each case.

Tetrahedral Si2-O distances (Table 4) are unusual, with long distances associated with each basal O atom and a very short distance with the apical O atom. Similar distances were observed by Moore (1970) for leucophoenicite and Kato et al. (1989) for jerrygibbsite. Two distances, Si2–O5 and Si2–O6, must represent an average of Si2 with ½O²⁻ + ½OH⁻, depending on the presence or ab-

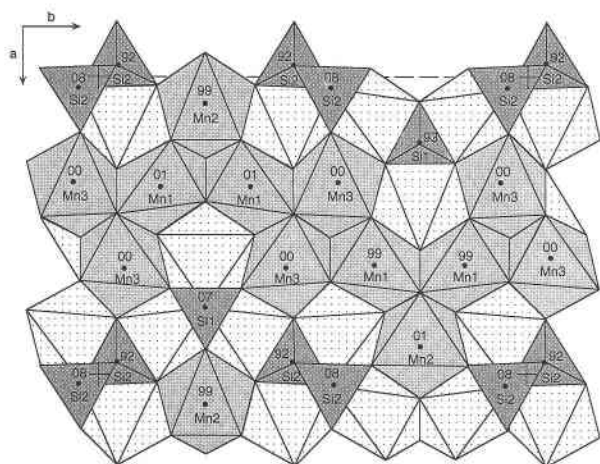Fig. 1. Polyhedral diagram of the ribbeite structure, projected down the c-axis. Numerical values are z coordinates in hundredths. The serrated edge-sharing chain of Mn octahedra centered at $z \approx 1.0$ is portrayed with an intermediate stipple and is superimposed on Mn octahedra (light stipple) centered at level $z \approx 0.5$. The Si tetrahedra centered at level $z \approx 1.0$, both fully occupied, isolated units and half occupied, edge-sharing pairs, are shown in darker stipple.
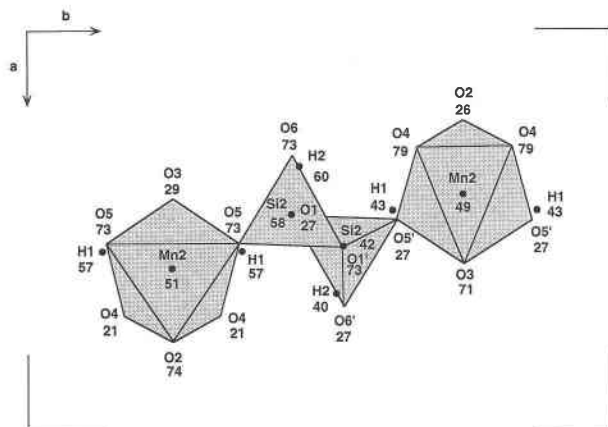

Fig. 2. Polyhedral diagram of a portion of the ribbeite structure centered at level $z \approx 0.5$ projected down the c axis and showing the relationship of H atoms to Mn octahedra and Si tetrahedra. Numerical values are z coordinates in hundredths.

sence of Si2, as discussed above. Support for this comes from anisotropic displacement parameters: U_{22} for O5 suggests an anisotropic ellipsoid elongated along b; U_{11} for O6 suggests an anisotropic ellipsoid elongated along a. The remaining two Si-O distances are associated with O1 (Fig. 2). As noted above, when Si2(0.58) is absent, O1 forms H bonds with O5 and O6 and an oxide bond with Si2(0.42), at a distance of 1.761(3) Å. When Si2(0.58) is present, H bonds are not formed, and the Si2-O1 distance contracts to 1.522(3) Å to satisfy valence requirements. Thus the position of O1 is constrained by satisfying two bonding patterns, depending on the presence or absence of Si2.

As noted earlier, the structures of alleghanyite and ribbeite are indeed related by a glide-plane unit-cell twin operation, as proposed by Kato et al. (1989). In terms of the nine original designations for unit-cell twinning given by Ito (1950), this is a G^2, or alternate, glide operation. Using the polyhedral diagram of alleghanyite given by Rentzeperis (1970), the serrated edge-sharing chain of Mn octahedra in ribbeite can be generated by a $c/4$ glide in alleghanyite repeated in the G^2 mode. In the ribbeite structure (Fig. 1), this glide is parallel to a. The fully occupied, isolated Si tetrahedral site in ribbeite can also be generated by this glide; however, only one of the disordered, edge-sharing pair of Si tetrahedra in ribbeite, the upward-pointing member in Figure 1, is generated. Valence needs of O atoms disrupted by the glide operation are met with H bonding. If the glide operation is G^1, or *en echelon* (Ito, 1950), the reverse situation occurs: the downward-pointing member of the disordered pair is produced, with the valence needs of O atoms again fulfilled by H bonding. Thus, it appears that the disordered edge-sharing tetrahedra in ribbeite are a direct consequence of a mixed-glide operation: statistically, half of the glides are alternate, half are *en echelon*. We do not know if the glide types are randomly mixed or if they occur in a regular pattern; in either case, the simultaneous occurrence of both types is designated G^3, or complex, in the notation of Ito (1950). We suggest that the leucophoenicite structure may be related to that of manganhumite by complex-glide unit-cell twinning, as defined by Ito (1950). It is interesting to note that Kato et al. (1989) did not observe half-occupied, edge-sharing pairs of tetrahedra in jerrygibbsite, a structure based on only an alternate glide. Jerrygibbsite may be a unique member of the leucophoenicite group; alternatively, the high R-factor (0.088) obtained by Kato et al. (1989) may indicate that the structure is partially in error, and that a refinement based on a structure with half-occupied edge-sharing tetrahedra may converge to a smaller residual.

ACKNOWLEDGMENT

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