

LETTER

The 10 Å phase: Crystal structure from single-crystal X-ray data

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ABSTRACT

Here we report the results of the first three-dimensional refinement of the 10 Å phase performed with single-crystal X-ray data.

The 10 Å phase, $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2\text{H}_2\text{O}$, is monoclinic, space group $C2/m$, $a = 5.323(1)\text{Å}$, $b = 9.203(1)\text{Å}$, $c = 10.216(1)\text{Å}$, $\beta = 99.98(1)^\circ$, $V = 492.9(2)\text{Å}^3$; the calculated density, assuming $Z = 2$, is $2.676\text{ g}\cdot\text{cm}^{-3}$. The structure has been solved by direct methods and refined by least-squares method with anisotropic displacement parameters. The final agreement index (R_1) was 0.088 for 54 refined parameters and 499 unique observed reflections collected with a diffractometer with a CCD detector.

The structure of the 10 Å phase is very similar to that of a homo-octahedral, 1 *M* trioctahedral mica: it is a silicate consisting of 2:1 tetrahedral-octahedral layers parallel to (001). The mean Si-O, Mg1-O, and Mg2-O bond lengths are 1.626, 2.082, and 2.081 Å, respectively. The ditrigonal rotation angle α is 0.53° . The interlayer of the 10 Å phase is occupied by water molecules. According to the oxygen occupancy, 1 H_2O p.f.u. is assumed in the investigated sample. Although the average water oxygen position is in the mid-plane, structural refinement suggests disorder along c^* . Twelve hydrogen bonds are located between the water molecule and the 6 + 6 oxygen atoms of the basal rings of adjacent tetrahedral sheets (water-oxygen distances averaging 3.19 Å). Therefore there are six possible orientations for the water molecule, with six hydrogen bonds pointing toward the upper basal ring and six pointing toward the lower ring of tetrahedral sheets. The orientational disorder of water, in agreement with previous Raman spectroscopy data, is a feature relevant to the evaluation of thermodynamic functions and thermal stability of the 10 Å phase, which is a possible water carrier (9.1 wt%) in subducting slabs at high pressure.

INTRODUCTION

The 10 Å phase, $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2\cdot x\text{H}_2\text{O}$, is a dense hydrous magnesium silicate that forms from talc at pressures between 3–5 GPa (Yamamoto and Akimoto 1977; Pawley and Wood 1995). Recently Perrillat et al. (2004), with real-time X-ray diffraction data, followed the mineralogical reactions of antigorite breakdown. They showed that, in the range 1.5–5 GPa, the dehydration of serpentine is temperature-dependent and above 550 °C forsterite and a phyllosilicate close to the talc structure nucleates. In complex ultramafic systems and compositions approaching natural Iherzolite a 10 Å phase structure forms at the expense of chlorite starting from 4.8 GPa, 680 °C, contributing significantly to the water budget in subduction zones (Fumagalli and Poli 2005).

Although the relevance of the 10 Å phase has been supported by experimental studies, the knowledge of its crystal structure is so far restricted to X-ray powder diffraction data, thermal analysis, and infra-red and micro-Raman spectroscopy performed on high pressure synthetic samples (Yamamoto and Akimoto 1977; Bauer and Sclar 1981; Fumagalli et al. 2001); all investigations generally agree within a layer-silicate nature of the 10 Å phase. On the basis of X-ray powder data and micro-Raman

spectroscopy performed using large platy hexagonal crystals of the 10 Å phase, Fumagalli et al. (2001) combined a mica-like stacking ($d_{001} = 9.64\text{--}10.07\text{ Å}$ compared to the 9.34 Å stacking of talc) as indicated by X-ray powder data and talc-like T-O-T layers and interlayer molecular water as indicated by micro-Raman spectroscopy. The occurrence of hydronium (H_3O^+) is not supported by Raman spectroscopy. On the contrary, the occurrence of water molecules in the interlayer is strongly suggested by the H_2O bending mode at 1593 cm^{-1} and two OH stretching modes at 3593 cm^{-1} and 3668 cm^{-1} in addition to the OH stretching of structural hydroxyl groups at 3622 cm^{-1} (Fumagalli et al. 2001). Micro-Raman spectra give an indication of partial static disorder in the orientation of the water molecules. Moreover, none of the three peaks in the OH stretching region agrees with the stretching mode frequency of hydronium in micas (White and Burns 1963).

Miller et al. (1991) hypothesised, from thermogravimetric data and calculation of dehydration enthalpies, that O^{2-} occupies the interlayer site and is stabilised by two resonating protons leading to momentary formation of OH, H_2O , and H_3O^+ , without direct interaction with neighbouring OH groups.

The structure of the 10 Å phase has recently been studied from neutron powder diffraction data (Pawley et al. 2004); the results from a deuterated 10 Å phase further confirm that a phlogopite-like model fits the measured spectra better than a

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talc-like model.

The amount of extra water that may be hosted by the 10 Å phase is debatable and values of x of 0.65 (Wunder and Schreyer 1992), 1 (Bauer and Sclar 1981), and 2 (Yamamoto and Akimoto 1977) have been proposed. However Fumagalli et al. (2001), on the basis of the swelling behavior of the 10 Å phase upon acetone treatment and its relation to the duration of the experiment suggested that time dependent hydration of the 10 Å phase is responsible for the variable amount of water that can be accommodated within the structure.

Recently Wang et al. (2004), used molecular dynamic calculations to propose different models for the 10 Å phase as a function of water content and P/T conditions, reflecting changes in the hydrogen configuration.

In spite of several techniques applied to model the 10 Å phase, and partly because of difficulties in synthesising suitable crystals, the crystal structure of the 10 Å phase has not yet been solved by X-ray single-crystal diffractometry. Now we report the results of the first X-ray three-dimensional refinement of the 10 Å phase performed using an exceptionally crystalline experimental product obtained by high-pressure multi-anvil synthesis; this was performed at the Dipartimento di Scienze della Terra, Milan, at 6.7 GPa and 650 °C (synthesis time = 360 h). Microanalysis of the sample yielded a MgO:SiO₂ ratio of 3:4 (Fumagalli et al. 2001). For further details on the high-pressure experimental techniques, including the starting material and assembly set up, see Fumagalli et al. (2001).

EXPERIMENTAL METHODS

Many crystals of the 10 Å phase were examined by single-crystal X-ray diffraction. They generally showed a poor crystal quality, with intergrowth and stacking faults giving spurious peaks and streaks along c^* . The sample used had dimensions of $0.06 \times 0.06 \times 0.005$ mm. Since area-detectors allow more reliable three-dimensional integration of diffuse reflections, the single-crystal diffraction data collection was carried out under room conditions with an XCALIBUR Oxford Diffraction diffractometer equipped with a CCD detector (Sapphire 2, 92 mm diagonal active area, $1k \times 1k$ pixels). Details of the data collection and refinement are reported in Table 1. The specimen is monoclinic, with the following cell parameters (from 1047 reflections indexed on the CCD): $a = 5.323(1)$ Å, $b = 9.203(1)$ Å, $c = 10.216(1)$ Å, $\beta = 99.98(1)^\circ$, $V = 492.9(2)$ Å³. The calculated density, assuming a cell content of $2[Mg_3Si_4O_{10}(OH)_2 \cdot H_2O]$, is $d_{calc} = 2.676$ g·cm⁻³. The lattice is C centered, and the possible space groups, on the basis of systematic extinctions, are $C2/m$ or Cm . On the basis of the lattice and chemical similarities with the phlogopite polytype 1 M , the first was assumed for the structural determination, and later confirmed as correct by the results of the analysis. After Lorentz, polarization, and empirical absorption

TABLE 1. Data, experimental, and refinement details for the 10 Å phase

Chemical formula	Mg ₃ Si ₄ O ₁₀ (OH) ₂ ·H ₂ O	Scan type	ω/ϕ
Space group	C2/m	Step size (°)	0.7
Lattice parameters	$a = 5.323(1)$ Å $b = 9.203(1)$ Å $c = 10.216(1)$ Å	No. of frames	1023
		Time/frame (s)	80
		No. measured refl.	3009
		No. independent refl.	890
	$V = 492.9(2)$ Å ³	No. observed refl.	499
Z	2	No. parameters	54
Density (calc.)	2.676 g/cm ³	R_{int}	0.061
Absorption coefficient μ	0.88 mm ⁻¹	$R_{obs} (F > 4\sigma)$	0.088
Crystal size (mm)	0.06×0.06×0.005	R_{all}	0.124
Diffractometer type	Oxford Diffr. CCD Xcalibur	wR^2	0.280
Radiation	MoK α (graphite monochr.)	Goof	0.973
θ range (°)	2–33	Largest diff. peak and hole	2.08 and –1.39 e/Å ³

corrections using the SADABS package (Sheldrick 1996), the discrepancy factor among symmetry related reflections was $R_{int} = 0.061$. The structure was solved by direct methods using the SIR97 package (Altomare et al. 1999). The refinement was carried out with anisotropic displacement parameters using SHELXL-97 (Sheldrick 1997). During the last stage of refinement, a difference Fourier synthesis showed some residuals which could be interpreted as due to a shift of atoms by $\pm b/3$ with respect to the basic structure. This can be interpreted as a consequence of random stacking faults with a $b/3$ component. This kind of disorder is a common feature of layer silicates and micas (see Brigatti and Davoli 1990 for biotite; Oberti et al. 1993 for preiswerkite; Mellini et al. 1996 for Cs-ferriannite; Cesare et al. 2003 for Ti-rich biotites). This feature could also be interpreted as $[310]$ microtwinning or $2M_1$ domains in a $1M$ dominant crystal. Oberti et al. (1993) showed that the elimination of the spurious peaks is possible by separately rescaling the reflections with $k \neq 3n$, which being affected by streaking are systematically underestimated.

None of the atoms showed anomalous displacement ellipsoids with the exception of the water oxygen atom O5, which has quite high displacement parameters with strong ellipticity. The principal mean square atomic displacements U of O5 are 0.19, 0.07, and 0.04 Å² and the ellipsoid is elongated in the $[001]$ direction. Taking into account this evidence, in the final stage of the refinement two models were tested; one with a fully occupied oxygen site in the mid-plane of the interlayer (model I) and another with two half-occupied O5 sites split along the c axis (model II). Model II yielded a O5–O5 distance of 0.54 Å. The final agreement indices of the two models were nearly equal and therefore cannot be distinguished.

In both models the hydrogen atom of the hydroxyl group O4 and those of the water molecule O5 could not be observed on the difference map and were not included in the refinement.

The final agreement index (R_1) was 0.088 for 54 refined parameters and 499 unique reflections with $F_o > 4\sigma(F_o)$, and 0.124 for all 887 data (model I). For model II, R_1 was 0.089 for 56 parameters. Although the R_1 value is high, due to the quality of data, the atomic structure is believed to be fully reliable. The neutral atomic scattering factor values from the *International Tables for X-ray Crystallography* (Ibers and Hamilton 1974) were used. Final atomic coordinates and displacement parameters for model I are in Table 2. Observed and calculated structure factors (Table 3) are deposited.¹

RESULTS AND DISCUSSION

Selected interatomic distances and geometrical parameters for the 10 Å phase are listed in Table 4. Table 5 lists the results of bond-valence calculations according to Brown and Altermatt (1985). The values of the bond-valence sums for anions and cations are as expected and yield a good check on the reliability of the 10 Å structure.

It could be argued from the similarities in lattice parameters, the structure of the 10 Å phase is very similar to that of a trioctahedral $1M$ mica: it is a layer silicate consisting of 2:1 tetrahedral-octahedral layers parallel to (001) (Fig. 1). The only difference

¹For a copy of Table 3, document item AM-05-016, contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. Deposit items are available on the American Mineralogist web site at <http://www.minsocam.org> (or contact MSA Business Office for updated link information).

TABLE 2. Fractional atomic coordinates and displacement parameters (Å²) for the 10 Å phase

Atom	x	y	z	U_{eq}
Si	0.5768(4)	0.1666(2)	0.2305(2)	0.018(1)
Mg1	0	1/2	1/2	0.018(1)
Mg2	0	0.8335(4)	1/2	0.020(1)
O1	0.8089(12)	0.2487(7)	0.1751(6)	0.022(1)
O2	0.5571(18)	0	0.1755(9)	0.021(2)
O3	0.6291(10)	0.1674(6)	0.3901(6)	0.015(1)
O4	0.1325(15)	0	0.3947(9)	0.016(2)
O5	0	0	0	0.099(10)

Note: O4 is the OH group; O5 is the water molecule.

from the phlogopite structure is in the interlayer, since in the 10 Å phase a water molecule occupies the site which in mica is occupied by potassium. In the structure of the 10 Å phase, this site between two adjacent 2:1 T-O-T layers is the only site with dimensions compatible with the size of the water molecule. A computation with the program CAVITY (Mugnoli 1992) shows that the radius of the cavity at 0, 0, 0 is 1.8 Å, while no other cavities with radii greater than 0.9 Å were found.

The tetrahedral sheet consists of Si-O tetrahedra sharing three vertices each to form an ideally hexagonal net. The Si-O distances are in the range 1.606(7)–1.638(7) Å, mean value 1.626 Å; the tetrahedral volume is 2.21 Å³. The tetrahedra are quite regular with angles in the range 108.9(4)–110.0(4)°, the angle variance is 0.493 deg². The tetrahedral sheet thickness is 2.162 Å.

The octahedral sheet consists of M1 and M2 octahedra sharing edges and occupied by Mg. As in mica, one M1 octahedron links two OH groups in trans configuration, while M2 coordinates two OH in cis position. The structure is homo-octahedral, the mean Mg1-O and Mg2-O bond lengths being 2.082 and 2.081 Å respectively. The octahedral flattening angles Ψ are 58.4° for M1 and M2, the octahedral thickness is 2.180 Å.

In the 10 Å phase, because of its synthetic composition, there are no substitutions at the octahedral and tetrahedral sites, which are completely filled by Mg and Si. The ditrigonal rotation angle α is 0.53°, a very low value, showing a small departure of the structure from the ideal hexagonal oxygen packing of the sheets and the small misfit between tetrahedral and octahedral sheets. Hazen and Wones (1972) showed that there is an inverse rela-

tionship between the rotation angle α and the mean ionic radius (R) of the octahedrally coordinated atoms; when R reaches 0.76 Å, the α rotation is 0°. In the 10 Å phase the radius of the octahedral cation is 0.72 Å, and α is indeed very low. Its value is in fair agreement with that obtained substituting the dimensional misfit $\Delta = 0.382$ Å of 10 Å phase in Toraya (1981) relationship: $\alpha = 33.90 \Delta - 9.854$. It is among the lowest measured for phyllosilicates (see Fig. 5 in Ishida et al. 2004)

The water molecule is located in the interlayer, and refinement of the site-scattering value indicates a complete occupancy of the site by oxygen. Therefore the occupancy of water was fixed at the value $x = 1$ H₂O m.p.f.u. The water oxygen atom O5 shows quite high displacement parameters and strong ellipticity. This feature is indicative of a likely positional disorder of the oxygen atom, depending on the different hydrogen bonds formed with the basal oxygen atoms of the tetrahedral sheets. The distance between O5 and O4 (the hydroxyl oxygen atom) is 3.971(9) Å. With this distance a direct interaction between the hydroxyl ion and the water molecule is unlikely, and, likewise, it is unlikely that a H₃O⁺ group might be formed by proton exchange. On the contrary hydrogen bonds could form with the basal oxygen atoms. Even if direct localization of the water hydrogen atoms was not possible, due to the data quality and to the very low hydrogen scattering factor, indirect considerations are possible

TABLE 4. Selected interatomic distances (Å) and geometric parameters for the 10 Å phase

Si-O1	1.631(7)	α (°) *	0.53(6)
Si-O1	1.638(7)	Δz (Å) †	0.004(9)
Si-O2	1.630(4)	V_T (Å ³)	2.21(2)
Si-O3	1.606(7)	Tetrahedral sheet thickness (Å)	2.162
<Si-O>	1.626	V_{M1} (Å ³)	11.9(7)
Mg1-O3 ×4	2.091(8)	V_{M2} (Å ³)	11.9(7)
Mg1-O4 ×2	2.063(6)	Octahedral sheet thickness (Å)	2.180
<Mg1-O>	2.082	Ψ_{M1} (°)	58.42(6)
Mg2-O3 ×2	2.082(7)	Ψ_{M2} (°)	58.41(7)
Mg2-O3 ×2	2.095(6)	$V_{O(5)^{III}}$ (Å ³)	65.0(8)
Mg2-O4 ×2	2.065(7)	$V_{O(5)^{VI}}$ (Å ³)	42.9(8)
<Mg2-O>	2.081	Interlayer thickness (Å)	3.526
O5-O1 ×4	3.179(7)	Δ (Å) §	0.382
O5-O2 ×2	3.188(9)		
O5-O1 ×4	3.199(7)		
O5-O2 ×2	3.200(10)		

* α is the angle of tetrahedral rotation.

† Δz was calculated as $[(z_{O1} + z_{O1})/2 - z_{O2}] c \sin \beta$ (Güven 1971).

‡ Ψ is the octahedral flattening.

§ $\Delta = 2\sqrt{3} \langle O-O \rangle_{\text{bas}} - 3\sqrt{2} \langle M-O \rangle$.

TABLE 5. Bond-valence calculations for the 10 Å phase

	Si	Mg1	Mg2	H1	H2	H3	Σ anions
O1	0.98 0.96 [0.98 0.96]				0.007 ×8 [0.007 ×2]	0.007 ×8 [0.007 ×2]	1.97
O2	0.98 [0.98 0.98]				0.007 ×4 [0.007 ×2]	0.007 ×4 [0.007 ×2]	1.99
O3	1.05 [1.05]	0.34 ×4 [0.34]	0.34 ×2 [0.34] 0.35 ×2 [0.35]				2.08
O4		0.37 ×2 [0.37]	0.37 ×2 [0.37 ×2]	1.00 [1.00]			2.11
O5					0.92 [0.92]	0.92 [0.92]	1.84
Σ cations	3.97	2.10	2.12	1.00	1.00	1.00	

Notes: Parameters were taken from Brese and O'Keeffe (1991). For the hydrogen bond, we used the bond-valence-bond-length correlation of Brown (1976), i.e., 0.08 for O...H. The values in square brackets are the contributions to the balance of anions.

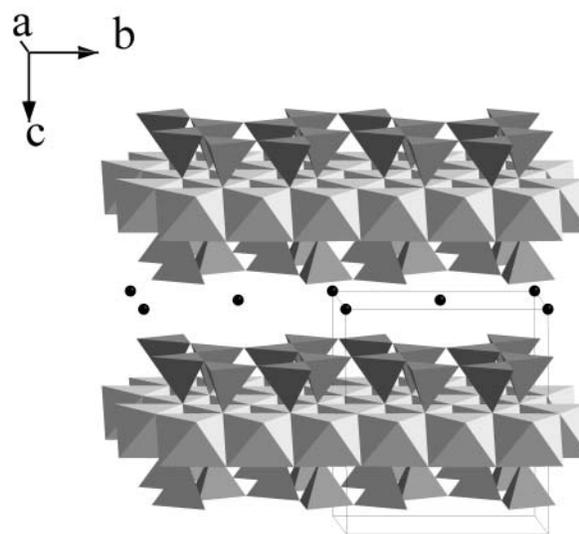


FIGURE 1. The structure of the 10 Å phase projected along an axis near [100].

on the basis of the “framework” configuration. There are six shorter (four equivalent O1-O5 and two O2-O5, mean value 3.182 Å) and six slightly longer (four O1-O5 and two O2-O5, mean value 3.199 Å) distances between O5 and the basal oxygen atoms of the 2:1 layers. The angles between the two opposing oxygen atoms of each sixfold basal ring and O5 are 112.9(2)° and 112.9(3)° respectively for the O1-O5-O1 and the O2-O5-O2 angles. Hydrogen bonds might therefore form with various orientations between the oxygen of the water molecule and the basal oxygen atoms of the tetrahedral sheets. There are six possible orientations for the water molecule, with six hydrogen bonds pointing toward the upper basal ring and six pointing toward the lower ring of an adjacent tetrahedral sheet (Fig. 2). Since these possible configurations are energetically equally favorable, the water molecules are randomly oriented in different positions. On the basis of the O-O distances, if interlayer water oxygen atoms occupy the 12 coordinated site, i.e., are located in the middle of the interlayer plane, the possible hydrogen bonds between interlayer water molecules and basal oxygen atoms are weak, but the hydrogen bond strengths can be stronger taking into account the positional displacement of O5 along the *c* axis, as shown by the apparent thermal ellipsoid and tested by the refinement cycles (model II). Indeed, in this latter model the lengths of the six shorter hydrogen bond fall in the range 3.01–3.09 Å.

The orientational disorder of water is consistent with the Raman spectra which show a broadening of the OH bands at 3593 and 3668 cm⁻¹ (Fumagalli et al. 2001). This feature should be relevant to the evaluation of thermodynamic functions and thermal stability of the phase.

The interlayer separation is 3.526 Å, which is greater than that of the Mg-rich micas (3.45–3.48 Å; Brigatti and Guggenheim 2002). This is expected, since size and charge of the interlayer constituents strongly affect the interlayer separation and the *c*-parameter of the unit cell. There is an inverse relation between tetrahedral rotation α and interlayer separation (see Fig. 15 in Brigatti and Guggenheim 2002), with several exceptions to the

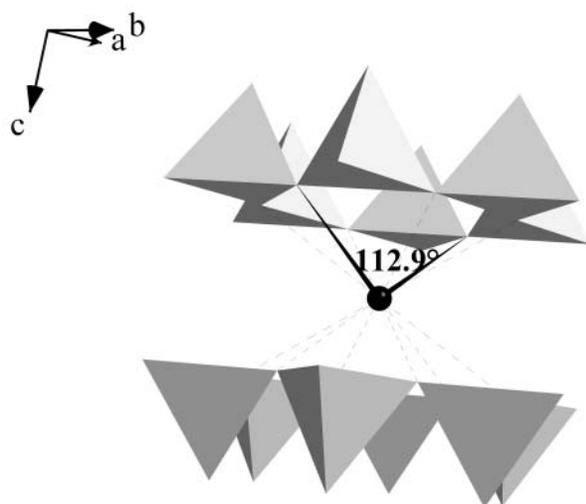


FIGURE 2. The environment of the water molecule, with the possible 12 hydrogen bonds (dotted lines). One of the six possible orientations of H₂O is indicated by underlining two hydrogen bonds with heavier lines.

direct relation (Ishida et al. 2004). The interlayer thickness of the 10 Å phase, is shorter than that predicted by applying the general relationship. This may be partly related to the interaction between the water molecules and the basal oxygen atoms. A similar behavior was observed in norrishite (Tyrna and Guggenheim 1991), where the narrow interlayer region was ascribed to the Coulombic interaction of O²⁻ at the O4 site and the interlayer potassium.

The structure of the 10 Å phase should be stable at high pressure. The compressibility of the 10 Å phase (Pawley et al. 1995) is strongly anisotropic, as expected for layer silicates. The [001] direction is by far the most compressible. As in phlogopite (Comodi et al. 2004), in the 10 Å phase the maximum deformation should affect the interlayer region. In phlogopite the T-O-T thickness decreases by less than 1% at 6 GPa, whereas the interlayer thickness decreases of about 13%. Therefore, assuming a similar behavior for the 10 Å phase, we can speculate that at high pressure the reduction of interlayer thickness strengthens the hydrogen-bond system, improving the stability of the phase. Moreover, when the pressure increases, in mica the larger octahedra compressibility with respect to that of tetrahedra induces an increase in the α rotation, which is needed to reduce the misfit. The increase of α with pressure tends to destabilize the mica structure. In fact, a large α rotation, which pushes together tetrahedral and octahedral cations, increases the electrostatic energy. As a result, those crystal-chemical mechanisms which reduce the α rotation will determine which structures are able to support higher pressures. In the case of the 10 Å phase, the octahedral and tetrahedral compositions allow a very low α rotation, warranting a greater baric stability. Furthermore the substitution of potassium by a water molecule eliminates the repulsion between the interlayer cation and the proton of the hydroxyl group, so reducing another possible way of structure destabilization at high pressure.

In conclusion, the refinement results of the 10 Å phase confirm the chemical formula Mg₃Si₄O₁₀(OH)₂H₂O; and the phase is a possible water carrier (9.1 wt%) in subducting slabs at high pressure.

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