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Combined in situ X-ray diffraction and Raman spectroscopy on majoritic garnet inclusions in diamonds

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Abstract

Mineral inclusions in Sao Luiz diamonds have been characterized using angle dispersive X-ray diffraction and Raman spectroscopy. We identified two different garnet phases coexisting with an omphacitic pyroxene. They represent disintegration products of a former homogeneous majorite-rich garnet phase. The two garnets have significantly different cell parameters but are tightly intergrown with their unit cells parallel to each other. The garnets are oriented relative to the diamond host with $[100]_{\text{garnet}}$ parallel to $[110]_{\text{diamond}}$. Combining the measured cell parameters of the garnet inclusions with chemical analyses of similar inclusions from the same source allows the extraction of a residual pressure between 1 and 3 GPa, depending on the exact chemical composition assumed. Depth-resolved Raman spectra at the diamond–garnet interface indicate a residual pressure of about 1 GPa. Such a low residual pressure is unexpected at first glance for a garnet assemblage from the transition zone. The inclusion pressure is lowered due to pyroxene crystals, which surround the garnet inclusions and act as cushions reducing the residual inclusion pressure. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: diamond inclusions; majorite; omphacite; transition zone

1. Introduction

Mineral inclusions in diamonds represent a unique source of information for the mineralogical composition of the Earth's mantle. Previous

reports of diamond inclusions describe the minerals olivine, pyroxene, and garnet [1,2] as well as various sulfides as main constituents. More recent studies on diamonds from the Kankan district in Guinea (West Africa) report Ca-silicates exhibiting the titanite structure [3], which seem to be the natural equivalent to material previously synthesized at high pressure [4]. Similar work on diamonds of Sao Luiz, Brazil [5], found assemblages of majorite-rich garnets, possibly Mg-Si-perov-

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skite, and (Mg,Fe)O, which are typical for transition zone and lower mantle compositions. Several garnet crystals from diamond inclusions were reported to have a pyroxene component dissolved [6–8]. The coexistence of a pyrope-grossular garnet with a jadeite-rich pyroxene phase is believed to represent an exsolution of the pyroxene component out of a majoritic garnet. This interpretation is based on the tight intergrowth observed for these inclusions [7–10] and the pressure stability limits of a pyroxene component dissolved in garnet [11–15].

With the exception of an energy dispersive X-ray diffraction experiment by Conrad et al. [16], all previous studies on garnet–pyroxene assemblages in diamond inclusions were done on recovered samples. This has the advantage of allowing precise chemical analyses but has the disadvantage that it prevents retrieving any information on possible residual pressure on the inclusion. This information, however, represents the most direct evidence for the pressure of inclusion and thus depth of inclusion. Moreover, *in situ* non-destructive measurements have to be promoted and developed for such rare samples. Inclusions are extremely difficult to extract from their diamond host and routine techniques have to be developed to first select the best-suited inclusions and then collect the maximum structural information before extraction, which can be destructive to the inclusions.

In this paper we report an *in situ* study on a garnet–pyroxene assemblage included in a diamond retrieved from the Sao Luiz alluvial deposit in Brazil [7,8,17]. The combined use of angle dispersive X-ray diffraction and Raman spectroscopy techniques allowed the unambiguous identification of the inclusion minerals (garnet and clinopyroxene). Combining this information with chemical analyses of very similar but extracted inclusions allowed the determination of a residual pressure. Comparing these results with residual pressures estimated on the basis of the different bulk moduli and thermal expansion of diamond and garnets, respectively, shows that the effective recorded residual pressure of such assemblages is lower than would be expected from the difference

in elasticity between diamond host and guest silicates.

2. Experimental

2.1. Samples

The diamonds studied were found in the alluvial deposits on the Sao Luiz river (Brazil), near the Aripuena kimberlite province in Brazil [7]. They contain associations of inclusions with compositions indicating derivation from the mantle transition zone and lower mantle. The previous studies were mainly focused on the inclusions which might originate from the lower mantle [5,7]. Special attention was paid to the association in the same diamond of (Mg,Fe)O (magnesiowüstite) and (Mg,Fe)SiO₃ pyroxene which might represent the former assemblage (Mg,Fe)O (magnesiowüstite)+(Mg,Fe)SiO₃ perovskite, which is thought to be the major paragenesis of the Earth's lower mantle. Beside this type of mineralogical associations, the Sao Luiz diamonds also contain garnet and garnet–pyroxene inclusions [7,8]. These inclusions are visually identified by optical microscopy as orange to pale orange garnets as found in an eclogitic paragenesis. In the present paper we have studied such a sample (labeled ZIL4). The sample, a 1.5 mm × 1.5 mm × 2.8 mm sized diamond, contains two garnet inclusions (~90 × 90 × 100 μm) in contact with each other: a pale orange one and a pale yellow to whitish one. One of them is rimmed by a light green mineral which resembles an eclogitic pyroxene. Such textures are frequently encountered around former majoritic garnet inclusions. The garnet phases are optically isotropic under crossed Nicols. After the various *in situ* experiments, an attempt was undertaken to extract the small inclusions from the diamond host. This resulted in a loss of the first inclusion. To prevent the loss of both crystals, we abandoned extracting the crystals. Instead, we tried to compensate the lack of direct chemical information by inferring possible chemical compositions from previously extracted inclusions from

the same locality with very similar visual appearance.

2.2. X-ray diffraction

Monochromatic ‘single’ crystal X-ray diffraction data were collected on beamline ID11 of the European Synchrotron Radiation Facility (ESRF) from inclusions of sample ZIL4. An X-ray beam (300 μm diameter) of 0.4858 Å wavelength was selected with two independent Si(111) monochromators. Wavelength as well as sample to detector distance was calibrated using a MgF_2 standard crystal. A peltier-cooled SMART CCD centered at $2\theta = 29^\circ$ with a calibrated sample-to-detector distance of 5.843 cm was used as detector. The active area of the detector had a diameter of 10 cm.

The inclusions were centered visually using a $10\times$ objective on a κ -geometry diffractometer. The centering procedure was difficult because of the lack of parallel faces on the diamond hosts. The refractive index of the diamond therefore introduced a significant error in the crystal centering. Diffracted beam centering [18] was not applicable due to the lack of four-circle diffraction geometry at the station during the time of the experiment. This problem caused a partial loss of intensity as a function of setting angles. This, combined with the very strong anisotropic absorption as well as extinction effects, both caused by the big diamond hosts, prevented us from fully exploiting the intrinsic potential of angle dispersive single crystal diffraction, namely the accurate refinement of a structural model.

Data were collected between $-180^\circ < \varphi < +180^\circ$ for four Ω settings at 0° , 60° , 120° and 270° , respectively. The step size in φ between two frames was 0.36° , leading to a total of 4000 frames. These frames were analyzed using the SMART software [19]. The combined presence of reflections from four or more inclusion crystals in addition to the very strong reflections from the diamonds prevented any application of automatic indexing. Orientation matrices for the diamond and the inclusion crystals had therefore to be determined by selectively picking individual peaks by hand. This turned out to be a tedious task, since peak ap-

pearance or profiles could not be used as a distinguishing feature. Mixing of reflections from different crystals was therefore unavoidable and spoiled most attempts at determining a UB matrix for any individual crystal. We nevertheless succeeded in finding the orientation matrix for two garnet crystals. Unfortunately, we were not so successful with the pyroxene reflections, which we recognized on the basis of their d values. It was obvious from some very closely separated peaks of low intensity that there are several pyroxene crystals present, all of them considerably smaller than the garnet crystals. This is in accordance with the macroscopic appearance of this type of inclusions [8].

2.3. Raman spectroscopy

Raman spectra of the inclusions were recorded with a XY Dilor© Raman microspectrometer equipped with a CCD detector. The spectrometer was used in backscattering geometry. The excitation laser beam (488 or 514 nm exciting lines of a Spectra Physics® Ar⁺ laser) was focused down to a 3 μm spot on the inclusion through the diamond with a 15 mm working distance $50\times$ objective (Mitutoyo©). The backscattered Raman light was collected through the same objective. Typical recording conditions necessary for obtaining good quality Raman spectra were of the order of 5–10 min. The presence of a confocal pinhole at the entrance of the spectrometer ensures a good filtering of the Raman and fluorescence signal of the diamond host.

3. Results

3.1. X-ray diffraction

The diffraction experiment revealed diffraction spots of several crystals. Based on d values, these reflections could be attributed to two different minerals, namely a garnet and an omphacitic clinopyroxene. For two garnet crystals, an orientation matrix was found, which gave significantly different volumes for the two crystals (Table 1). For both cases, triclinic refinements of the

Table 1

(A) Chemical compositions of diamond inclusions similar to the one investigated in this work. (B) Observed UB matrices and cell parameters for the two garnet crystals and refined cell parameters for the pyroxene crystal

	gaMj1	gaMj2	ga gaIb	ga gaIb4	gaMjm6	gaMjm7
(A)						
Ca-majorite	0.24	0.44	0.00	0.01	0.11	0.27
Pyrope	0.18	0.20	0.49	0.48	0.36	0.20
Andradite	0.03	0.02	0.05	0.01	0.11	0.05
Almandin	0.21	0.21	0.27	0.28	0.22	0.22
Grossular	0.27	0.01	0.15	0.18	0.13	0.26
Spessartin	0.07	0.13	0.01	0.01	0.07	0.00
a (Å)	11.64	11.56	11.23	11.28	11.62	11.64
K (GPa)	176.38	178.79	172.20	173.56	175.83	176.58
K'	4.20	4.34	4.16	4.24	3.97	4.45
V_0	1576.84	1546.10	1415.24	1436.15	1567.54	1575.90
V_0/V_{Gar1}	1.02	1.00	0.91	0.93	1.01	1.02
P_{Gar1} (GPa)	3.28	-0.31	-12.88	-11.17	2.16	3.18
V_0/V_{Gar2}	1.01	0.99	0.90	0.92	1.00	1.00
P_{Gar2} (GPa)	0.96	-2.48	-14.29	-12.69	-0.09	0.85
(B)						
UB (Garnet-1)	0.08362233	0.01918162	-0.00687993			
	-0.01588808	0.04317299	-0.07274355			
	-0.01276076	0.07194526	0.04548631			
a (Garnet-1) (Å)	11.619(1)					
UB (Garnet-2)	0.08416770	0.01877729	-0.00476477			
	-0.01388726	0.04367193	-0.07320790			
	-0.01350679	0.07210871	0.04557841			
a (Garnet-2) (Å)	11.578(3)					
a, b, c, β (pyroxene)	9.61(1)	8.84(1)	5.22(1)	106.8(1)°		

The values for cell parameter a , bulk modulus K and its first pressure derivative K' as well as the zero pressure volume V_0 were interpolated from the respective end-member values according to the chemical composition.

orientation matrices are in agreement with cubic metric (Garnet-1: $a = 11.618(3)$, $b = 11.622(3)$, $c = 11.617(3)$, $\alpha = 89.96(1)$, $\beta = 90.01(1)$, $\gamma = 89.97(1)$; Garnet-2: $a = 11.571(3)$, $b = 11.568(3)$, $c = 11.567(3)$, $\alpha = 90.06(1)$, $\beta = 89.99(1)$, $\gamma = 89.96(1)$). The final refinement was therefore done with cubic constraints. Apart from these two garnet crystals there exists at least a third garnet crystal in the inclusion. Various attempts to sort out its orientation matrix failed. No such matrix could be determined either for any of the clinopyroxenes. This is mainly due to the impossibility of separating reflections of the various pyroxene crystallites from each other but also from the garnet crystals. Strong diamond reflections, which create Umweg diffraction spots, added further complication in classifying individual reflections.

Comparing the UB matrices of the garnets with each other as well as with the orientation of the diamond host reveals not only a significant differ-

ence in cell parameters for the two garnet crystals, but also a nearly parallel orientation within the diamond host with the $[100]_{\text{garnet}}$ parallel to $[110]_{\text{diamond}}$. This suggests a recrystallization of the garnets while included in the diamond lattice.

The cell parameters corresponding to the two garnets for which an orientation matrix could be refined are given in Table 1. Refined cell parameters from the d values of those reflections, which were attributed to pyroxene, are also given in Table 1.

3.2. Raman spectroscopy

The three minerals identified by X-ray diffraction could also be recognized by Raman spectroscopy. The two largest crystals (orange and pale orange) have Raman spectra characteristic of majoritic garnets (Fig. 1). Majoritic garnets ($\text{Si} > 3$) have a characteristic Raman signature in the fre-

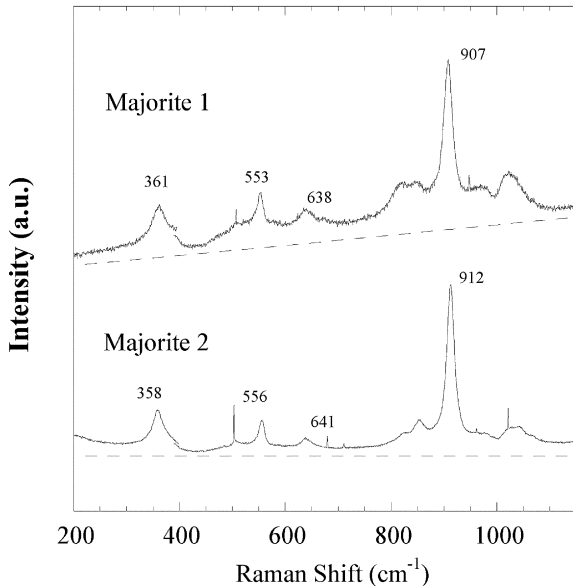


Fig. 1. In situ Raman spectra of the two garnet inclusions investigated in this work. The broad feature between 800 and 900 wavenumbers in combination with the Si–O stretching signal above 900 cm^{-1} are characteristic for garnets containing a majoritic component. The slight differences of the two Raman spectra confirm the interpretation of the observed difference in unit cell parameters to be due to slight chemical differences.

quency region of the SiO_4 – SiO_6 stretching vibrations: a broad peak is observed between 800 and 900 cm^{-1} just before an intense band (900–930 cm^{-1}) classically assigned to Si–O stretching vibrations of the SiO_4 tetrahedra in all known garnets. The spectra of the two majoritic garnets present differences (Fig. 1) in the frequency of the most intense band and the background fluorescence which can be attributed to chemical differences. Raman spectra characteristic of omphacitic pyroxenes are recorded at the rim of the garnets (Fig. 2).

4. Discussion

The interpretation of in situ data with respect to residual pressure is impossible in the absence of additional chemical constraints. In our case, however, chemical information could be obtained by chemical analyses on very similar inclusions pre-

viously extracted from diamonds of the same source (Table 1). The results obtained from our in situ experiments can thus be discussed in terms of these possible chemical compositions. When combining the measured chemistries with the cell parameters obtained from this study, one finds negative pressures for four of the six chemical compositions. For the other two samples (gaMj1 and gaMjm7), one obtains residual pressures for the two garnets of about 3 and 1 GPa, respectively (Table 1). There are two possible explanations for the two different cell volumes and thus residual pressures of the two measured garnet crystals. Either the two majoritic garnets have – for some (e.g. kinetic) reason – lost their pyroxene component and thus recrystallized during different instances of the ascent, or the two garnets ended up at a slightly different chemical composition, i.e. lost different fractions of the pyroxene component. The fact that the two garnet crystals are closely intergrown and thus have an almost parallel orientation within the diamond lattice allows us to reject the first hypothesis. We therefore assume that the chemical composition for garnet-2 is different from garnet-1. This assumption is corroborated by the results of the depth-dependent Raman spectroscopy experiments and the

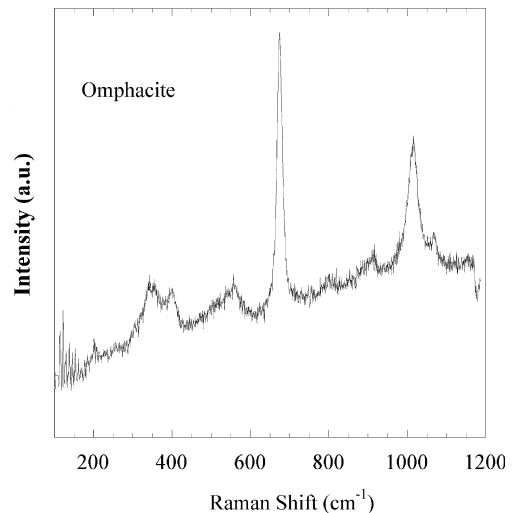


Fig. 2. In situ Raman spectra of the material surrounding the garnet inclusion. It can be identified as omphacite in accordance with d values measured with the diffraction experiment.

Table 2

Thermoelastic parameters used to estimate an expected residual pressure of our observed assemblage

	Diamond		gaMj1		gaMjm7		Majorite	
K_0 (GPa)	444	[23]	176	[23]	176	[23]	166	[24]
dK/dP	2.0	[23]	4.4	[23]	4.4	[23]	4.4	[24]
dK/dT (GPa K ⁻¹) [25]	-0.02		-0.02		-0.02		-0.02	
a_0	8.70×10^{-7}	[27]	2.07×10^{-5}	[26]	2.07×10^{-5}	[26]	3.00×10^{-5}	[26]
a_1	9.23×10^{-9}	[27]	2.50×10^{-9}	[26]	2.50×10^{-9}	[26]	2.50×10^{-9}	[26]
a_2	6.99×10^{-12}	[27]	-4.30×10^{-1}	[26]	-4.30×10^{-1}	[26]	-4.30×10^{-1}	[26]
$d\alpha/dP$ K ⁻¹ GPa ⁻¹	-5.00×10^{-7}	[26]	-7.80×10^{-7}	[25]	-7.80×10^{-7}	[25]	-7.80×10^{-7}	[25]
μ (GPa)	534	[28]						

$\alpha(T)$ is given as $\alpha(T) = a_0 + a_1(T-300) + a_2(T-300)^2$ for diamond and as $\alpha(T) = a_0 + a_1T - a_2T^{-2}$ for garnets. T in Kelvin.

color differences (pale orange and whitish) between the two crystals mentioned above. The Raman measurements yielded a shift of the diamond Raman vibrational mode at the diamond–garnet interface, which corresponds to a pressure around 1 GPa. This value is in good agreement with the result obtained from the lattice parameters of garnet-2 assuming a chemical composition similar to gaMj1 and gaMjm7. This suggests that the chemical composition of garnet-1 is richer in pyrope component. A change of the pyrope/grossular ratio of garnet-1 from $\sim 1/3$ (gaMj1, gaMjm7) to $\sim 3.5/1$ would yield a residual pressure of 1 GPa also for garnet-1, in accordance with the Raman data. The question remains why two closely intergrown garnets with almost parallel orientation have different chemical compositions. The most plausible explanation is that during the rapid ascent, the original majoritic garnet was split into two crystals at an early stage of the pyroxene exsolution process and the exsolution did not proceed to the same extent in the two separate crystals.

The observed residual pressure is in clear contrast to an expected residual pressure as calculated based on the differential bulk moduli and thermal expansion of diamond, majorite and grossular/pyrope garnet. In our case such calculations are slightly complicated by the fact that the observed assemblage represents an exsolution product from a majorite originally included in the transition zone but exsolved as inclusion in the diamond. It is nevertheless possible, using Eq. 1 slightly modified after [20], to obtain an estimate: for a given P, T combination of the diamond source, an

external pressure is calculated at which the included majorite crystal feels an inclusion pressure of ~ 10 GPa. This is the pressure at which majorite is expected to exsolve into pyrope/grossular and omphacite. Using this calculated value, we then calculate the expected inclusion pressure when the host diamond is under ambient conditions:

$$\int_{P_o}^{P_a} \frac{1}{K_D(P, T_o)} dP + \int_{T_o}^{T_a} \alpha_D(P_a, T) dP - \int_{P_{oi}}^{P_i} \frac{1}{K_i(P, T_o)} dP - \int_{T_o}^{T_a} \alpha_i(P_i, T) dP = \frac{3(P_i - P_a)}{4\mu_D} \quad (1)$$

In Eq. 1, subscripts i and D denote values for inclusion and diamond, respectively. P_o and T_o stand for external P and T at the ‘deep’ end of the integration. T_a and P_a denote the ‘shallow’ end of integration for external pressure and temperature. P_{oi} represents the ‘deep’ integration limit for the inclusion pressure (which is not the same as the external pressure for the case of the exsolution product). K is the bulk modulus, α the volumetric thermal expansion and μ_D the shear modulus of diamond. The latter was taken to be the Voigt–Reuss–Hill average of the shear modulus for an isotropic aggregate computed from the values c_{11} , c_{12} and c_{44} of diamond (Table 2). Although we are dealing with a single crystal, which is different from an isotropic aggregate, this simplifying assumption is justified through

the very isotropic properties of the elastic tensor of diamond (Schreuer, personal communication). Table 2 lists the values of the physical constants used for the calculations. The numeric solution of the Lambert W function arising from solving Eq. 1 for P_a or P_i was done using the Maple V (release 5) package.

We performed several runs for different possible inclusion pressures within the transition zone ($13 \text{ GPa} < P_o < 20 \text{ GPa}$). The corresponding temperatures were interpolated using the geotherm proposed by Anderson [21] as compiled in Poirier [22]. With this procedure, we obtain expected residual inclusion pressures between 5 and 6 GPa. These values are significantly higher than our observed value of 1 GPa. In fact, it is not possible to reproduce an inclusion pressure of 1 GPa under the assumption that the exsolution occurred while included in the diamond host. On the other hand, if we calculate a theoretical source pressure for a garnet of the observed chemical composition starting at an inclusion pressure of 1 GPa, we obtain pressures around 2 GPa. Since this is clearly below the stability limit of diamond we can infer that our measured inclusion pressure does not imply a shallow inclusion depth. We explain the observed discrepancy between observed and expected inclusion pressure by the fact that in our case the garnet crystals are not included as isolated crystals in the diamond host, but are embedded in an assemblage with a 'cushion' of pyroxenes and other garnets. This allows the garnet crystals to relax some of their inclusion pressure. It is very difficult to account for this cushioning effect in the model calculations mainly due to difficulties in determining exact volumetric ratios between pyroxene and garnet. The basic mechanism of such a cushioning effect, however, can be visualized through a simple one-dimensional model system consisting of two confined springs with different force constants, compared with a single confined spring. In the latter case, at a given compressional confinement Δx , a spring with force constant f_1 feels the force:

$$F_{1\text{spring}} = f_1 \times \Delta x \quad (2)$$

If on the other hand the confinement is occupied

by two different springs of different force constants, f_1 and f_2 , the same compressional confinement is distributed over the two springs: Δl for the spring with force constant f_1 and $(\Delta x - \Delta l)$ for the second spring with force constant f_2 . The individual force acting on each spring must be equal:

$$F_{2\text{springs}} = f_1 \times \Delta l = f_2 \times (\Delta x - \Delta l) \quad (3)$$

By substituting Δl it can be shown that:

$$F_{2\text{springs}} = f_1 \times [(f_2 \times \Delta x) / (f_1 + f_2)] =$$

$$F_{1\text{spring}} \times f_2 / (f_1 + f_2) < F_{1\text{spring}} \quad (4)$$

$F_{2\text{springs}}$ is thus smaller than $F_{1\text{spring}}$, since, by definition, both force constants are positive. The springs are thus experiencing a cushioning effect.

This simple, one-dimensional and linear reasoning holds also for the more complicated case of a three-dimensional compression using non-linear compressibility constants. The argument of the cushioning effect of course also relies on the fact that at the moment of the exsolution, the actual residual pressure of the inclusion aggregate corresponds to the equilibrium pressure of the assemblage. The larger volume of the two-phase aggregate compared to a single majorite phase is thus automatically buffered as long as kinetics and chemical composition allow for a progressive exsolution during the ascent of the host.

5. Conclusion

The investigated assemblage of inclusions from the transition zone consists of an omphacitic pyroxene tightly intergrown with two different garnets. The garnets differ mostly in their relative Ca/Mg ratio but have a parallel orientation and are built into the diamond lattice in an oriented way. Garnets show a residual pressure of around 1 GPa.

This residual pressure is in contradiction with a residual pressure expected for an assemblage exsolved from a majoritic garnet at an inclusion pressure around 10 GPa as it is expected for in-

clusions stemming from the transition zone. This discrepancy is due to a cushioning effect of the pyroxene rims surrounding the garnet crystals. Inclusion pressures derived from multiphase inclusions in diamonds should therefore be interpreted with great care, because the coexistence of various phases within a single inclusion can cause cushioning effects on the individual crystals.

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