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Ageing of low-firing prehistoric ceramics in hydrothermal conditions[#]

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Abstract

Remains of a prehistoric ceramic object, a moon-shaped idol from the Bronze Age found in archaeological site Zdiby near Prague in the Czech Republic, were studied especially in terms of the firing temperature. Archaeological ceramics was usually fired at temperatures below 1000 °C. It contained unstable non-crystalline products, residua after calcination of clay components of a ceramic material. These products as metakaolinite can undergo a reverse rehydration to a structure close to kaolinite. The aim of this work was to prove whether the identified kaolinite in archaeological ceramics is a product of rehydration. The model compound containing high amount of kaolinite was prepared in order to follow its changes during calcination and hydrothermal treatment. Archaeological ceramics and the model compound were treated by hydrothermal ageing and studied by XRF, XRD and IR analyses. It was proved that the presence of kaolinite in the border-parts of the archaeological object was not a product of rehydration, but that it originated from the raw materials.

Keywords*: prehistoric ceramics, characterization, ageing, kaolinite*

I. Introduction

Prehistoric ceramics were usually fired at temperatures below 1000 °C. They were produced mainly from natural raw materials, usually from local sources. The main components were quartz, micas, feldspars, carbonates, sometimes clay minerals (kaolinite, illite or/and montmorillonite) and products of calcination in the form of reactive non-crystalline phases depending on the firing temperature [1].

The most frequently studied clay mineral kaolinite ($Al_2Si_2O_5(OH)_4$) has a two-layer structure [2–9]. This structure is formed by silicon-oxygen tetrahedral layer and alumina octahedral layer, which alternate periodically [2]. Kaolinite changes to an unstable non-crystalline product, metakaolinite ($Al_2Si_2O_5$) at 600 °C. During this process the structure of kaolinite loses chemically bounded water (equation 1) [3].

$$Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O \rightarrow Al_2O_3{\cdot}2SiO_2 + 2H_2O \qquad (1)$$

This calcination product is able to rehydrate to a structure close to kaolinite at a temperature below 950 °C (equation 2) [4].

$$Al_2Si_2O_7 + (2\text{-}x)H_2O \rightarrow Al_2Si_2O_{5+x}(OH)_{4-2x} \qquad (2)$$

Similar equation is valid for another clay mineral, illite (equation 3) [4].

$$\begin{aligned} &K_{2-x}Al_4(Si_{6+x}Al_{2-x})O_{20}(OH)_4 \rightarrow \\ &\rightarrow K_{2-x}Al_4(Si_{6+x}Al_{2-x})O_{22} + 2H_2O \end{aligned} \qquad (3)$$

The presence of kaolinite can be identified by XRD, DTA and IR analysis. Characteristic positions of kaolinite peaks in infrared spectrum are found between 3600 and 3700 cm^{-1}. The bands at 3686, 3669 and 3651 cm^{-1} belong to inner-surface OH bonds and the peak at 3619 cm^{-1} belongs to inner OH bond for the ordered structure. Kaolinite with a lower degree of ordering has IR bands at 3669 and 3651 cm^{-1} substituted by one peak at the position 3650 cm^{-1} [5,6].

During the ageing process of a low-firing ceramics caused by the long time storage of an object under the ground, the metakaolinite rehydration to a structure close to kaolinite can occur. The natural ageing can be

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simulated in an autoclave in laboratory conditions by standardized test methods - f.e. French standard [10] and their modifications.

The aim of this work was to prove whether the identified kaolinite in the archaeological ceramics is a product of rehydration or that it originates from the raw materials. For this reason the measurements of the model compound were performed. The obtained results helped to clarify the behaviour of kaolinite during the ageing process.

II. Experimental

The ageing process was studied on the samples of archaeological ceramics and on the model compound. The prehistoric ceramic object (moon-shaped idol) from the Bronze Age (Fig. 1) was found in Zdiby, near Prague in the Czech Republic. The moon-shaped idol had trapezoidal shape (50 cm × 10 cm) and at the borders had horns [11]. The model compound was prepared to correspond to the studied samples of the archaeological ceramics in chemical and mineralogical composition. The model compound contained higher amount of kaolinite compared to archaeological samples in order to follow its changes during calcinations and subsequent hydrothermal treatment.

Powder samples of the archaeological ceramics and of the model compound were prepared in an agate mortar. Samples were calcined at 600 °C during 10 to 120 minutes for the model compound and 120 minutes for the archaeological ceramics (Zdiby C). After the calcination, the samples were treated in an autoclave by French standard method (5 h at 180 °C) and its modifications (24 h at 180 °C and 10 h at 230 °C), Table 1.

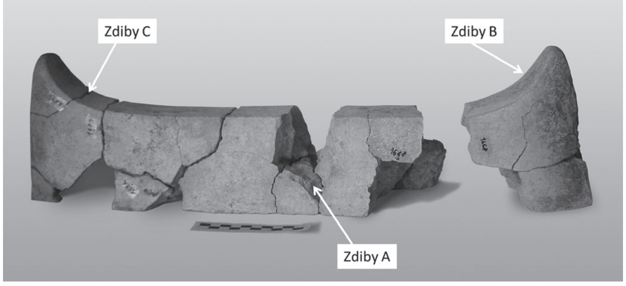

Figure 1. The moon-shaped idol from the Bronze Age found in Zdiby (photo by Z. Mazač)

Chemical composition of the samples was determined by X-ray fluorescence analysis (XRF- Sequential WD-XRF spectrometer ARL 9400 XP+). Phase composition of powder samples was identified by X-ray diffraction analysis in the range of 5–65° 2θ (XRD- Difractometer PANanalytical X´pert Pro with Cu anode). XRD patterns were evaluated by the program X´pert HighScore Plus and the appropriate database. For identification of OH bonds Infrared spectroscopy (IR-Spectrometer Nicolet IS 10, Thermo Scientific) was used. The spectra were measured by ATR crystal of ZnSe in the range of 4000–400 cm^{-1}. Data were evaluated by programs Omnic and Origin.

III. Results and discussion

Chemical compositions of the archaeological samples (A - central-part and B, C - border-parts) and of the model compound are shown in Table 2 and Table 3. The chemical compositions of the archaeological samples are slightly different. These differences are the result of inhomogenity of the ceramics materials, which is characteristic for archaeological ceramics.

Phase composition determined by XRD analysis is presented in Fig. 2 and in Table 4. The model compound contains quartz, mica (muscovite) and clay mineral (kaolinite). The three samples of archaeological ceramics contain quartz, micas (muscovite, sericite), feldspars (orthoclase, microcline, plagioclase) and clay mineral (as illite) as main mineral phases. Clay mineral kaolinite was identified only in the border-parts of the archaeological object (Zdiby B and C).

Table 1. The characteristic of the samples and realized experiments

Sample	Characteristic	Calcination	Hydrothermal ageing
Model compound	Mixture with higher amount of kaolinite	600 °C; 10, 20, 30, 40, 50, 60 and 120 minutes	5h 180 °C, 24h 180 °C, 10h 230 °C
Zdiby A	central-part of the object	-	24h 180 °C, 10h 230 °C
Zdiby B	border-part of the object - horn 1	-	-
Zdiby C	border-part of the object - horn 2	600 °C; 120 minutes	24h 180 °C, 10h 230 °C

Table 2. Chemical composition of the archaeological ceramics and of the model compound [wt.%]

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	Total
Model compound	50.0	46.7	1.1	0.3	0.4	0.3	1.1	0	99.9
Zdiby A (center)	68.0	22.2	3.5	0.9	1.5	1.0	2.3	0.2	99.6
Zdiby B (border 1)	68.0	22.7	3.4	0.9	1.1	1.3	2.1	0.2	99.7
Zdiby C (border 2)	67.7	22.5	3.5	0.9	1.3	1.3	2.2	0.2	99.6

Table 3. Chemical composition (trace elements) of the archaeological ceramics and of the model compound [wt.%]

	P_2O_5	V_2O_5	Cr_2O_3	ZnO	SrO	ZrO_2	BaO
Model compound	0.07	0	0	0.004	0	0.015	0
Zdiby A (center)	0.20	0.015	0.011	0.009	0.013	0.08	0.05
Zdiby B (border 1)	0.11	0.020	0.009	0.011	0	0.08	0.04
Zdiby C (border 2)	0.18	0.020	0.011	0.015	0	0.08	0.04

Table 4. Semi-quantitative analysis from the XRD patterns

	Mineralogical composition [wt.%]			
	quartz	micas/illite	feldspars	kaolinite
Model compound	**	***	-	****
Zdiby A (center)	***	***	***	-
Zdiby B (border 1)	***	***	***	*
Zdiby C (border 2)	***	***	***	*

**** very large, *** large, ** significant, * small, - non-identified

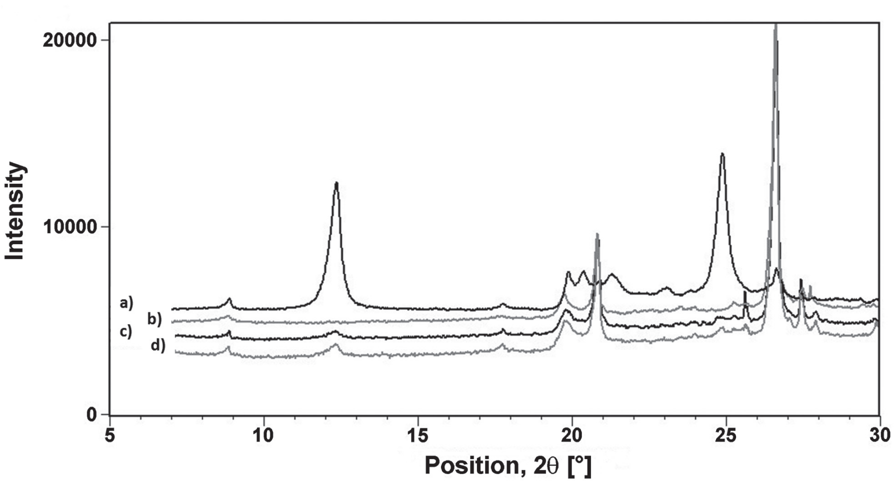

Figure 2. XRD patterns of: a) the model compound and the archaeological ceramics: b) Zdiby A, c) Zdiby B and d) Zdiby C

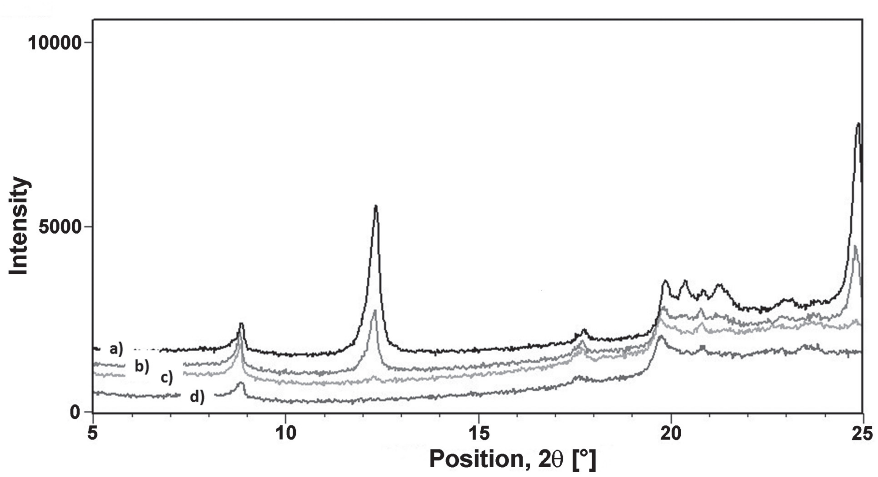

Figure 3. XRD patterns of the model compound after calcination at 600 °C for different times: a) 10, b) 20, c) 30 and d) 120 min

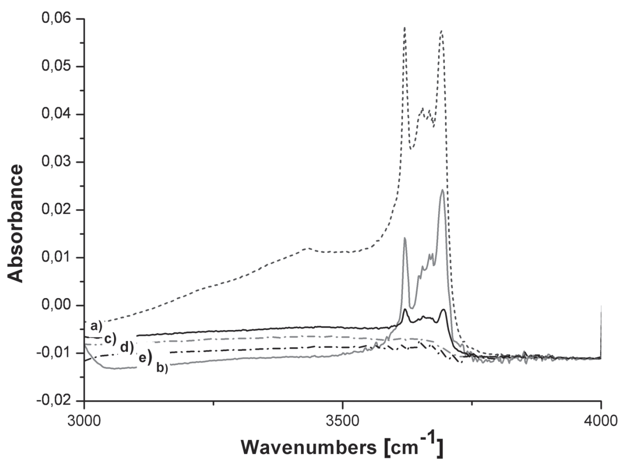

Figure 4. IR spectra of the model compound: a) uncalcined and calcined at 600 °C for different times: b) 10, c) 20, d) 30 and e) 120 min

The model compound (MC) was calcined at the temperature of 600 °C for different times (Fig. 3). The amount of kaolinite decreases with increasing the calcination time. After 30 minutes of calcination no kaolinite was identified in the sample by XRD analysis.

These changes were observed also by infrared spectroscopy in the range of 3000–4000 cm^{-1}, where the bands of the OH bonds of kaolinite can be found, Fig. 4. The sample calcined at 600 °C for 10 minutes had a high degree of the ordering of kaolinite structure, indicated by the positions of the bands at 3693, 3667 and 3654 cm^{-1}, which belong to inner-surface OH bond and the pick at 3620 cm^{-1}, which belong to the inner OH bond were identified. The sample calcined at 600 °C for 20 minutes showed lower degree of the structure ordering (band at 3655 cm^{-1}). After 30 minutes of calcinations no signs of ordering could be monitored.

The samples calcined at 600 °C for different times were subsequently treated hydrothermally in an autoclave

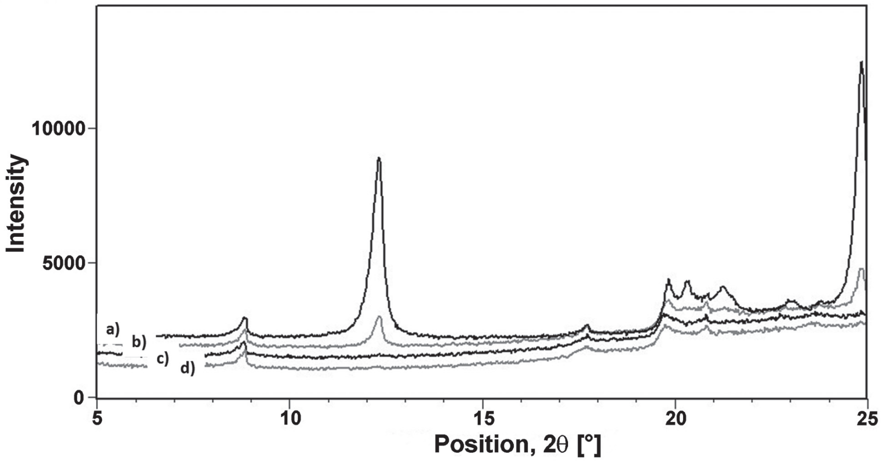

Figure 5. XRD patterns of the model compound after calcination at 600 °C and hydrothermal ageing for 5 hours at 180 °C for different times: a) 10, b) 20, c) 30 and d) 120 min

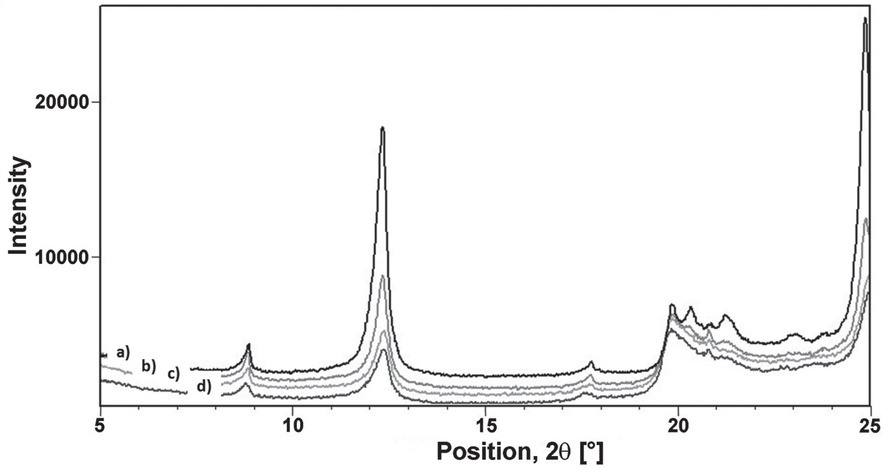

Figure 6. XRD patterns of the model compound after calcination at 600 °C and hydrothermal ageing for 10 hours at 230 °C for different times: a) 10, b) 20, c) 30 and d) 120 min

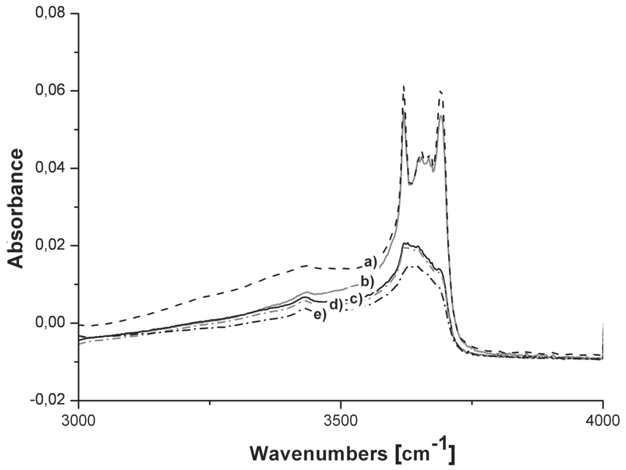

Figure 7. IR spectra of the model compound hydrothermal ageing for 10 hours at 230 °C: a) uncalcined and calcined at 600 °C for different times: b) 10, c) 20, d) 30 and e) 120 min

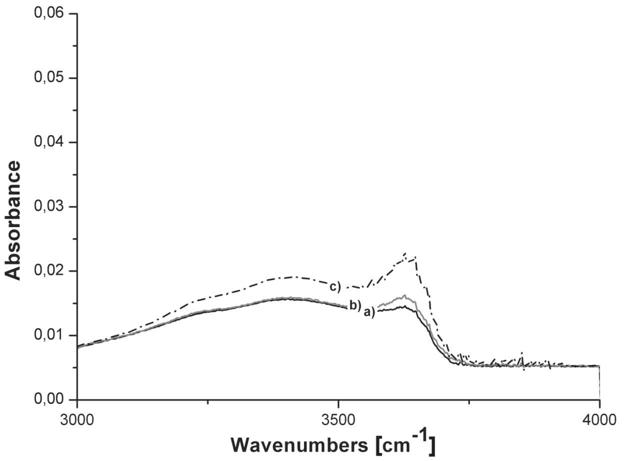

Figure 8. IR spectra samples from the central-part of archaeological ceramics Zdiby A: a) untreated and hydrothermal ageing b) 24 h at 180 °C and c) 10 h at 230 °C

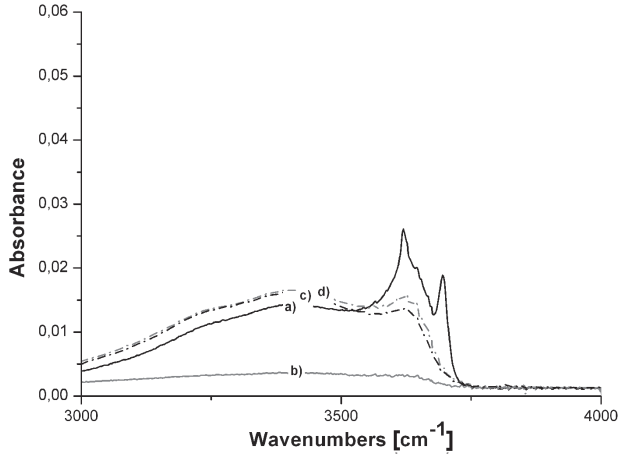

Figure 9. IR spectra of the border-part of archaeological ceramics Zdiby C: a) untreated, and after b) calcination at 600 °C for 120 min and hydrothermal ageing c) 24 h at 180 °C, d) 10 h at 230 °C

according the French standard method (5 h at 180 °C) and also at higher temperature (10 h at 230 °C). Figure 5 shows XRD study of the effect of calcination time on the rehydration process of kaolinite during hydrothermal treatment at 180 °C. The samples with the calcination time longer then 30 minutes did not rehydrate to kaolinite structure. When harsher conditions were used (10 h at 230 °C) the reverse hydratation was monitored in all studied samples of the model compound, Fig. 6. Results of IR spectroscopy (Fig. 7) showed that only sample calcined at 600 °C for 10 minutes had high degree of the structure ordering. In other samples containing kaolinite according XRD analysis (Fig. 6) the ordered structure was not proved.

The hydrothermal ageing by the French standard method did not have the effect of reverse rehydration in the model compound with calcination time longer than 30 minutes, so the samples of prehistoric ceramics where long firing time can be presumed were treated only by harsher conditions (10 h, 230 °C). The central-part (A), which did not contain kaolinite in the original (untreated) sample, was subjected to the hydrothermal ageing. The presence of kaolinite after the hydrothermal ageing was not confirmed by either IR or XRD analyses. Compared to the original sample, no changes were registered even after the hydrothermal ageing for 24 hours at 180 °C. The efforts to produce the reverse rehydration were not successful until the hydrothermal ageing 10 hours at 230 °C was used, Fig. 8. The calcined samples from the border-parts did not contain kaolinite even after the hydrothermal ageing at 230 °C for 10 h, Fig. 9. In Fig. 10 XRD spectra of the original and the treated samples of the archaeological ceramics are compared. The analyses proved the presence of kaolinite only in the border-part (C) of the original sample.

IV. Conclusions

The results prove that the presence of kaolinite in low-firing ceramics depends not only on the temperature but also on the calcination time. The unstable non-crystalline residues of clay minerals have the ability to rehydrate. The degree to which this takes place depends on the conditions of the hydrothermal ageing. Using the normalized conditions of the hydrothermal treatment the rehydration to the original crystalline structure was not observed. If higher temperatures (230 °C) and longer times (10 h) are applied the rehydration can be monitored.

Comparing the results of the hydrothermally treated samples of the model compound and of the studied low-firing prehistoric ceramics, a moon-shaped idol, it can be concluded:

- kaolinite identified in the border-parts of the object was from the raw materials (primary source) and is not a product of the rehydration,
- the border-parts were exhibited to a temperature lower than 450–600 °C,
- the presence of the primary kaolinite in both border-parts of the object and its absence from the

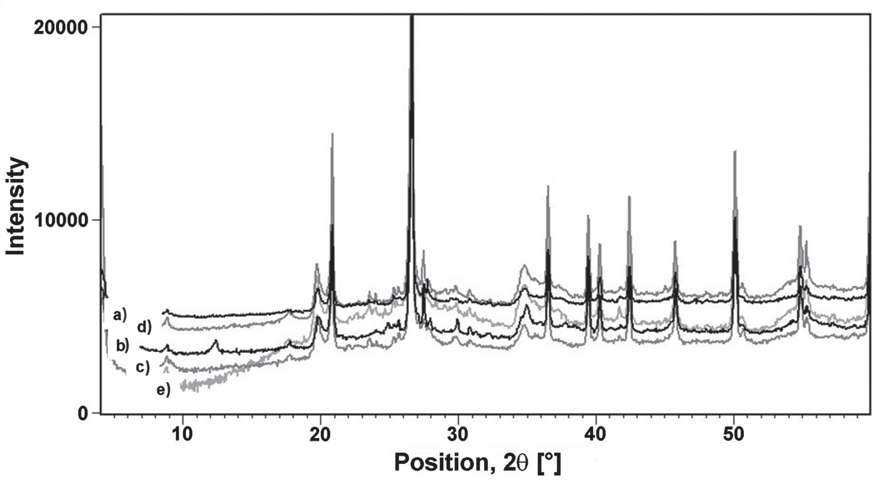

Figure 10. XRD patterns of the archaeological ceramics: a) untreated Zdiby A, b) untreated Zdiby C, c) Zdiby C after calcination at 600 ° C for 120 min, d) Zdiby A after hydrothermal ageing at 230 °C for 10 h and e) Zdiby C after hydrothermal ageing at 230 °C for 10 h

central-part proved, that the object was not fired uniformly, probably during its exposure to an open fireplace.

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