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Calcium Phosphate Glasses and Glass-ceramics for Medical Applications

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Abstract

Since natural bone is predominantly hydroxyapatite, $Ca_5(PO_4)_3OH$*, synthetic calcium phosphate materials are perfectly biocompatible when used in the human body environment. This paper presents the results of a study of the effects of microstructure and processing conditions on the mechanical behaviour of some calcium phosphate glasses. The bend strength of* $Ca(PO_3)_2$ *glass was found to be strongly dependent on the fabrication process. Rapid cooling generates surface compression that increases the strength from 125 to 217 MPa. The addition of alumina (5 wt%) increases the fracture toughness from 4·6 to 7·8 MPa m*$^{1/2}$*. A lower strength of 70 MPa, but a higher* K_{IC} *of 17 MPa m*$^{1/2}$ *was obtained from the crystallized glass-ceramic; both changes result from the microstructural anisotropy of the crystallized glass.*

Natürliche Knochen bestehen hauptsächlich aus Hydroxylapatit, $Ca_5(PO_3)_3OH$*, weshalb synthetische Kalziumphosphate im menschlichen Körper sehr gut biokompatibel sind. Dieser Artikel berichtet über die Effekte der Mikrostruktur und der Herstellungsbedingungen auf die mechanischen Eigenschaften von einigen Calziumphosphatgläsern. Die Biegefestigkeit von* $Ca(PO_3)_2$*-Glas zeigt eine starke Abhängigkeit vom Herstellungsprozess. Hohe Abkühlraten erzeugen Druckspannungen in der Oberfläche, wodurch die Festigkeit von 125 auf 217 MPa ansteigt. Die Zugabe von 5 Gew.-%* Al_2O_3 *führt zu einem Anstieg der Bruchzähigkeit von 4·6 auf 7·3 MPa m*$^{1/2}$*. Eine geringere Festigkeit von 70 MPa, aber mit einem höheren* K_{IC} *von 17 MPa m*$^{1/2}$ *verbunden, wurde an kristallisierten Glaskeramiken gemessen. Die genannten Änderungen resultieren von den Mikrostukturanisotropien im kristallisierten Glas.*

L'os naturel étant composé de façon prédominante d'hydroxyapatite $Ca_5(PO_4)_3OH$*, les matériaux synthétiques à base de phosphate de calcium sont parfaitement biocompatibles pour une utilisation à l'intérieur du corps humain. Dans cette publication, on a étudié les effets de la microstructure et des conditions de préparation sur le comportement mécanique de certains verres de phosphate de calcium. La résistance à la flexion d'un verre de* $Ca(PO_3)_2$ *dépend fortement du procédé de fabrication. Un refroidissement rapide génère une compression de surface qui élève la résistance de 125 à 217 MPa. Un ajout d'alumine (5% en poids) élève la ténacité de 4·6 à 7·3 MPa m*$^{1/2}$*. Une vitrocéramique cristallisée présente une résistance inférieure (70 MPa) mais un* K_{IC} *plus élevé (17 MPa m*$^{1/2}$*); ces deux changements proviennent de la microstructure anisotrope du verre cristallisé.*

1 Introduction

The most commonly used biomaterials for load bearing joint prosthesis are metallic alloys[1] e.g. Co–Cr alloys, stainless steel, Ti–Al–V alloys, and high density/ultra high molecular weight polyethylene (UHMWPE).[2] The metallic alloys were chosen because of their high strength, toughness, and good corrosion resistance; polyethylene is the usual counterface material since it provides a low coefficient of friction as well as good shock-absorbing properties and so avoids damage to the surrounding tissue. The attachment of the prosthesis to bone is achieved by bone cement (polymethyl methacrylate).

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However, these materials are only adequate for short-term joint replacement since they can loosen and sometimes corrode in service in the highly stressed and corrosive environment of the human body.[3] The corrosion and, more particularly, the attachment problems have led to the development of other biomaterials. Ceramics such as alumina, with their excellent tribological properties and high strength, have been shown to give good performance.[4] However, their use is still limited, due to problems such as their inherent brittleness, low fatigue resistance and the slowness and inhomogeneity of bone ingrowth into the prosthesis.

Since bone is mainly composed of calcium, oxygen, phosphorus and organic tissues, calcium phosphate materials are usually considered biocompatible and even bioactive, i.e. new living bone is generated by chemical resorption of the biomaterial. A strong attachment is therefore quickly developed through bone ingrowth and reaction with the material.[5] Although calcium phosphate ceramics[6] and glass-ceramics[7,8] have excellent biomedical behaviour, their poor strength and brittleness limit their use in load-bearing medical applications.

The purpose of this study was (a) to determine if calcium phosphate glasses ($Ca(PO_3)_2$) with and without small additions of Al_2O_3 and ZrO_2 have suitable mechanical properties to enable them to be used as biomaterials in the locomotor system, and (b) to investigate the crystallization behaviour of these glasses with the aim of forming useful monolithic glass-ceramics.

2 Materials and Experimental Procedure

The calcium phosphate starting powder was purified $Ca(H_2PO_4)_2 \cdot H_2O$ with impurity levels of $<0{\cdot}005\%$ Cl, $<0{\cdot}05\%$ SO_4^{2-} and $<0{\cdot}015\%$ Fe. The water dissociation, glass transition and crystallization peak temperatures were determined with a differential scanning calorimeter (DSC). The water dissociation temperature was found to be 450°C. Small additions of high purity alumina and zirconia powders were made (see Table 1) to investigate their effect on the mechanical properties and crystallization behaviour of the glass. These materials were dry-milled, together with the calcium phosphate powder in a polythene container, using high purity alumina media.

Table 1. Chemical and physical characteristics of additives

Material	*Major impurities*	*Mean particle size (μm)*	*Specific surface area (m^2 g^{-1})*
Al_2O_3	0·04% Na_2O, 0·06% SiO_2 0·04% Fe_2O_3, 0·04% CaO	10	1
ZrO_2	0·9% SiO_2, 0·3% Al_2O_3 0·2% TiO_2, 0·06% Fe_2O_3	1·5	4

2.1 Sample preparation

The powder was carefully dried at 500°C prior to charging into an air furnace for melting in a platinum crucible. Since molten calcium phosphate tends to decompose with the volatilization of P_2O_5, the melting temperature has to be kept sufficiently low to minimize P_2O_5 losses but high enough to reduce the viscosity for casting. A temperature of 1200°C was found to be a good compromise, since the viscosity was low enough for casting and a weight loss of only $0{\cdot}2\%\ h^{-1}$ was measured.

A boron nitride (BN) mold was used to make 5 mm diameter rods for the four-point bend testing. To obtain perfectly annealed samples, the glass was poured into the preheated mold (570°C) and then maintained at the glass transition temperature for 10 min followed by slow cooling to room temperature. To determine the effect of the cooling rate on the mechanical properties, some samples were tested 'as cast', i.e. the glass being poured into a cold mold, resulting in rapid cooling, with no subsequent annealing treatment. Contamination of the glass by the BN mold was found to be negligible by chemical analysis.

2.2 Fracture toughness measurements

The fracture toughness measurements were performed using the Vickers indentation technique.[9–11] Fracture analysis is based on the propagation of a semi-circular or half-penny-like crack (Fig. 1) below

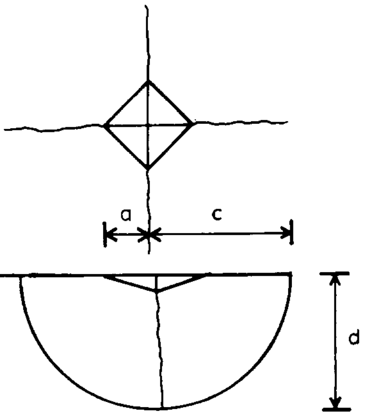

Fig. 1. Schematic diagram of crack geometry for a Vickers hardness indentation.

the indenter. The crack length at the indentation corner can be semi-empirically correlated to the plain strain fracture toughness K_{IC}.[11]

Two conditions have to be fulfilled for this technique to be valid: (a) a half-penny-like crack must be developed so that the crack length, c, is representative of the crack depth, d, and (b) the c/a ratio has to be greater than 2 to ensure that the crack crosses the plastic zone, where a is half the diagonal of the Vickers indentation. Residual stresses at the surface of the specimen, e.g. due to machining or fast cooling, are known to seriously affect the fracture toughness measurement. In the present study, specimens used for the fracture toughness determination were annealed, ground and then carefully polished down to 0·05 μm alumina. Some of the specimens were tested, annealed, and retested to determine the effect of the residual surface stresses left by the polishing. Each fracture toughness value is the average of the measurements from four indentations, i.e. 16 crack lengths. A comparison was then made with values of fracture toughness obtained from the more conventional single edge notch-beam (SENB) method.[12]

3 Results and Discussion

3.1 Elastic modulus

The elastic modulus (E) of pure calcium phosphate glass was determined to be 57 ± 2 GPa using the pulse–echo ultrasonic technique. This is closer to the elastic modulus of bone than conventional biomaterials (bone: $E = 17$ GPa, stainless steel: $E = 210$ GPa and high density alumina: $E = 400$ GPa). The similarity of the modulus of bone and that of the prosthesis is highly desirable to limit the stresses induced at the bone–implant interface during loading and the stress shielding effect through the prosthesis.[5]

3.2 Strength

The modulus of rupture (MOR) was obtained using a test jig with 50 mm and 15 mm outer and inner spans, respectively. The results for calcium phosphate glasses, with and without additions of alumina and zirconia are summarized in Table 2. It can easily be seen that the most important influence on strength is annealing after casting.

The high flexural strength for the as-cast specimens (217 MPa) arises from the surface compression generated during fast cooling. This effect is similar to that observed in silicate glasses.[13] The explanation is that the centre of the glass cools more slowly than the surface during rapid cooling and results in a difference in specific volume between the surface and interior. This causes the surface to be pulled into compression, hence a higher tensile stress is required to fracture the material.

Table 2. Modulus of rupture (MOR) values for glasses

Specimen	*Addition (wt %)*	*Number of tests*	*MOR (MPa)*	*Weibull modulus*
As-cast	Pure	3	217 ± 46	—
As-cast	1% ZrO_2	3	268 ± 44	—
Annealed	Pure	15	125 ± 35	3·8
Annealed	1% ZrO_2	11	125 ± 17	7·2
Annealed	2% Al_2O_3	10	94 ± 15	5·8

Casting the glass into a preheated mold and annealing allowed for stress relaxation to occur and eliminated the surface compressive stresses. This results in lower values for the flexural strength for the glass both with and without additions of Al_2O_3 and ZrO_2. Low Weibull moduli and scatter in the strength data were also observed in these glasses, even after annealing.

The modulus of rupture measured on the as-cast specimens are higher than that of bone (60–170 MPa). However, the strength may be degraded by slow, subcritical crack growth and dynamic fatigue under 'in-vitro' or 'in-vivo' conditions. Strength data must be obtained under these conditions to establish whether such degradation of properties occurs.

3.3 Fracture toughness and hardness

The Vickers indentation technique for fracture toughness measurement is applicable to calcium phosphate glasses since the cracks developed below the indenter have the required geometry (see Figs 2 and 3). However, as can be seen in Fig. 3, some lateral cracks can be observed. The energy used to create these cracks is not taken into account by the equation, since the measured variable is the surface crack length, representative of the half-penny crack only. The fracture toughness is therefore overestimated.

Comparison between Tables 3 and 4 indicates that the surface stresses induced by the polishing have a significant effect on the fracture toughness values since, on annealing, they were reduced by 13%, 48% and 34% for the pure glass, the 1% ZrO_2 glass and the 2% Al_2O_3 glass samples, respectively. The explanation for this is that grinding and polishing

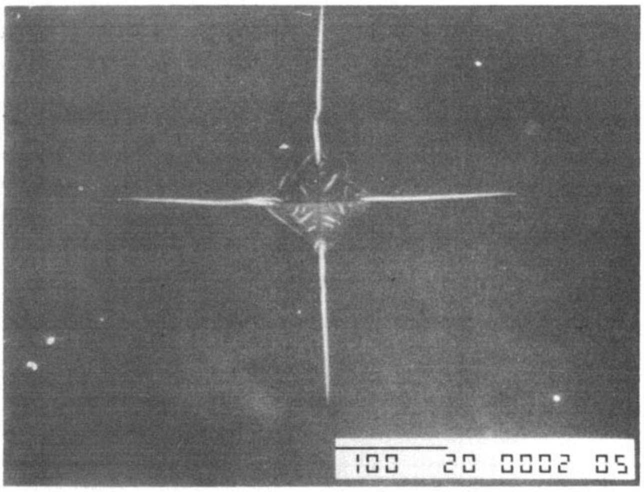

Fig. 2. Vickers indentation in pure calcium phosphate glass showing crack geometry.

Table 3. Fracture toughness of polished annealed glasses

Specimen	*Fracture toughness* (*MPa* $m^{1/2}$)	*Hardness* (*GPa*)
Pure	4·6 ± 0·2	3·5 ± 0·1
1% ZrO_2	7·2 ± 1·5	3·7 ± 0·2
2% Al_2O_3	5·4 ± 0·7	3·3 ± 0·3

Table 4. Fracture toughness of annealed glasses, polished and re-annealed

Specimen	*Fracture toughness* (*MPa* $m^{1/2}$)	*Hardness* (*GPa*)
Pure	4·0 ± 0·2	3·4 ± 0·1
1% ZrO_2	3·7 ± 0·2	3·6 ± 0·1
2% Al_2O_3	3·5 ± 0·4	3·3 ± 0·5

induces surface compression as a result of local heating. Since fracture toughness is inversely proportional to crack length, surface compression leads to an overestimate of K_{IC}. The fracture toughness determined by the Vickers indentation technique is a local fracture toughness, i.e. in this case, a typical half-penny radius varied from 0·1 to 0·2 mm. Therefore, the condition of the surface should be representative of the bulk material if the Vickers indentation technique is to be used with any degree of confidence. On the other hand, the hardness readings were not significantly affected by the surface compression and are similar to those reported previously.[14]

The effect of up to 5% addition of alumina on the fracture toughness of the glass was investigated. Results for the as-polished samples are given in Fig. 4. Additions of alumina increase the fracture toughness and the hardness of calcium phosphate glass from 4·6 to 7·8 MPa m$^{1/2}$ and from 3·4 to 4·1 GPa, respectively, for an addition of 5 wt% Al_2O_3. Although these values were measured on as-polished samples, and thus are not absolute values, they are still representative of the trend. It is very unlikely that this fracture toughness increase is due only to increasing surface compression since the rise in K_{IC} would not be so consistent.

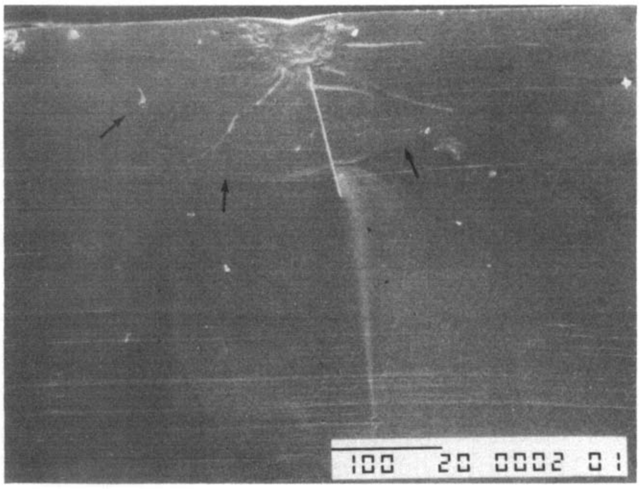

Fig. 3. Transverse section through a Vickers indentation showing lateral cracking.

The fracture toughness measured for the different calcium phosphate glasses is relatively high, e.g. $K_{IC} = 4{\cdot}0$ MPa m$^{1/2}$ for glass having a ratio $CaO{:}P_2O_5 = 1$, whereas normal K_{IC} values for silicate glasses lie between 0·6 and 1 MPa m$^{1/2}$. However, to confirm the validity of the fracture toughness determination by the Vickers indentation technique, SENB specimens were tested. A fracture toughness value of 4·3 MPa m$^{1/2}$ was obtained. Therefore, it was concluded that the Vickers indentation technique was suitable for bulk fracture toughness measurement of these glasses.

3.4 Crystallization of glasses

The crystallization behaviour of pure calcium phosphate was studied by Differential Scanning

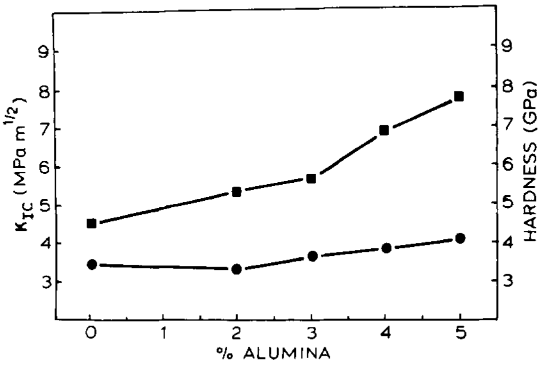

Fig. 4. Change in K_{IC} (■) and hardness (●) with alumina content.

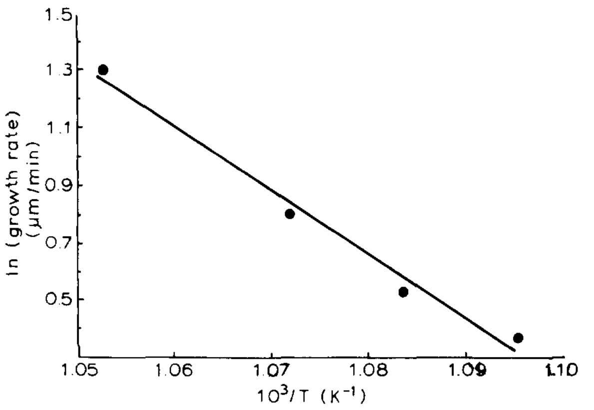

Fig. 5. Arrhenius plot of crystal growth rate for calcium phosphate glass.

Calorimetry (DSC). The crystal growth rate was determined from isothermal DSC runs made in the range 640–680°C on ground glass with a particle size distribution between 150 and 212 μm.

The Arrhenius plot of growth rate versus reciprocal temperature is given in Fig. 5. The activation energy for crystal growth above the glass transition temperature was found to be 427 kJ mol^{-1}. This value is in good agreement with that determined by Abe *et al.*[15] using hot stage microscopy. Since this value is similar to the energy needed to break the phosphorus–oxygen bond,[16] it is thought that crystallization occurs by breaking and rearranging these atomic bonds.

3.5 Glass transition and crystallization peak temperatures

The glass transition and the crystallization peak temperatures were investigated by DSC; the results are given in Table 5. The glass transition temperature (T_g) found for the pure calcium phosphate glass is significantly higher than that found by Abe *et al.*[15] There are two possible reasons for this discrepancy. Firstly, the difference in techniques used to determine T_g (since Abe *et al.* used thermal expansion curves) and secondly, the fact that, for both techniques, the value of T_g is dependent on the heating rate. Abe *et al.* report a value of T_g of 510°C (compared to 550°C in the present study) for an identical heating rate of 10°C min^{-1}. However, this difference is within the expected range when comparing the two different measurement techniques.[17] Furthermore, for glasses of the phosphate group, T_g can be lowered by the presence of residual hydrogen or hydroxyl groups,[18] so the glass prepared in this study may have had less combined water than the one prepared by Abe *et al.*

Table 5. Glass transition and crystallization temperature of different glasses

Material	*Glass transition temperature (°C)*	*Crystallization peak temperature (°C)*
Ca:P = 0·5	550	665
1% ZrO_2	550	700
1% Al_2O_3	550	700
2% Al_2O_3	550	710
5% Al_2O_3	570	760

The glass transition temperature is the temperature at which atomic motion becomes sufficient to allow stress relaxation to occur. Additions of small amounts of Al_2O_3 or ZrO_2 did not change T_g significantly (see Table 4). This implies that the structure and bonding in the glass are not altered by these low levels of additive and so do not change the thermal properties and viscosity of the glass. For higher amounts of alumina (5 wt%), there is an increase in T_g, since a significant amount of Al_2O_3 is incorporated in the glass network, thus leading to the formation of a stronger and more stable glass structure.

On the other hand, the crystallization peak temperature always increased in the presence of Al_2O_3 or ZrO_2 even for small additions (< 5 wt%). This might be explained by the fact that alumina and zirconia are intermediate oxides which are incorporated into the glass network and so tend to increase the stability of the glass; a situation similar to that observed in silicate glasses when intermediate oxides are introduced. Although the crystallization peak for the pure glass is 665°C, it is feasible to completely crystallize these glasses near the glass transition temperature, i.e. 570°C. The same crystalline phase, β-$Ca(PO_3)_2$, was confirmed by X-ray diffraction in both cases. No apparent change in cell dimensions was detected upon addition of Al_2O_3 or ZrO_2.

3.6 Glass-ceramic strength

The modulus of rupture of pure calcium phosphate glass crystallized at 570 and 665°C was found to be only 70 and 35 MPa, respectively. Such low values can be explained by the anisotropic microstructure[15] of the crystallized material which is shown as a fracture surface in Fig. 6. The glass-ceramic consists of bundles of crystalline fibres which are surface-nucleated and then grow perpendicular to the outer surface of the MOR bar across the sample. This forms a plane of weakness and therefore explains the poor strength of the crystallized glass.

Fig. 6. Fracture surface of calcium phosphate glass crystallized at 570°C.

The further reduction in strength of the material crystallized at the higher temperature of 665°C is attributed to the porosity generated during crystallization. Figure 7 shows the extensive microporosity which was observed in the fracture surface and is a result of significant shrinkage at this temperature. By contrast, this is not observed in the glass-ceramic crystallized at 570°C. The densities of both the glass and glass-ceramic crystallized at 570°C were 2·62 $\mathrm{Mg\,m^{-3}}$ indicating that no volume change occurred during low-temperature crystallization. This is due to the fact that the glass viscosity is so high at this temperature that no shrinkage can occur and so no density change and pore formation result. However, as a result, high internal stress is introduced,[15] and this might contribute to the poor strength of the glass crystallized at this temperature. The bulk density of the glass crystallized at 665°C was found to have decreased to 2·32 $\mathrm{Mg\,m^{-3}}$. A large amount of open porosity was found in addition to the microporosity and so explains the apparent decrease in overall density. It is clear that high temperature crystallization is not suitable for glass-ceramic formation.

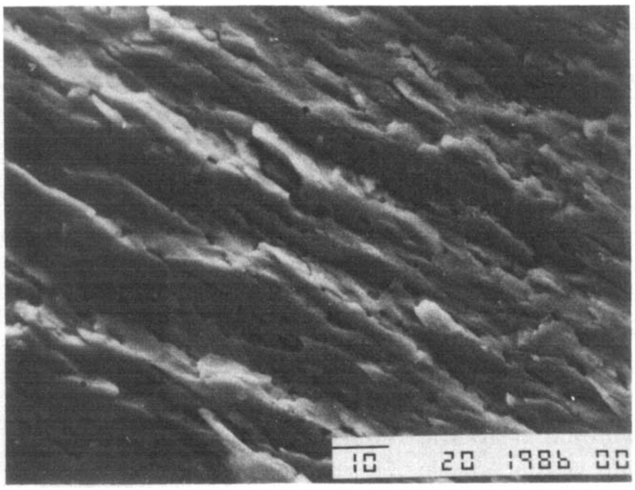

Fig. 7. Fracture surface of calcium phosphate glass crystallized at 650°C.

The fracture toughness of the glass-ceramic crystallized at 570°C was determined by the SENB technique (it was not possible to use the Vickers method due to sample anisotropy). A high value of 17 $\mathrm{MPa\,m^{1/2}}$ was obtained and this is attributed to the highly fibrous nature of the microstructure causing extensive crack branching and absorption of fracture energy.

4 Conclusions

(1) The strength of calcium phosphate glass ($Ca(PO_3)_2$) is affected by the cooling rate after casting. Annealed calcium phosphate glass has a flexural strength of 125 MPa. However, increasing the cooling rate generates surface compression, and significantly improves the flexural strength up to a value of 213 MPa.

(2) Despite the fact that alumina additions do not have a pronounced effect on the glass strength, they do modify its fracture behaviour, i.e. additions of 5 wt% of Al_2O_3 increase the fracture toughness of the glass by 70%.

(3) The poor strength but high K_{IC} of calcium phosphate glass-ceramics is attributed to the fibrous microstructure obtained after crystallizing near T_g. These materials are found to be highly anisotropic in behaviour.

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