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Surface behaviour of high MgO-containing glasses of the Si–Ca–P–Mg system in a synthetic physiological fluid

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Abstract

Two glasses of the Si–Ca–P–Mg system with low SiO_2 content (25 and 29 mol%) and high MgO contents (31 and 36 mol%, respectively) have been immersed in a Kokubo's synthetic physiological solution for different times up to 30 days. The surface modifications of the glasses were observed by SEM and the changes in the surface composition followed by EDS. ICP was used to assess the evolution of ionic concentrations in the solution, namely Ca and P.

It was observed that both glasses induced the precipitation of Ca–P rich layers on their surfaces, although these were poorly attached to the glass substrate. Ca and P ions required for the apatite formation were mainly provided by the composition of the glass, which was severely dissolved in the solution.

The observed apatite-forming ability of these glasses, notwithstanding their high MgO content, suggests that further improvements at the surface and in the glasses can lead to attractive potentially bioactive materials.

Keywords: Surfaces; Apatite; MgO; Biomedical applications

1. Introduction

The discovery of Bioglass[1] and of a new concept—bioactivity—opened a novel research area on glasses and glass-ceramics for bone repair and substitution.[1–8] Different types of bioactive materials are still under development and a great effort is being put in the understanding of the mechanisms and factors governing bioactivity.

The bioactive behaviour of glasses and glass-ceramics, identified as their capability for bone-bonding, is attributed to the formation of an apatite-like layer on their surface, with composition and structure equivalent to the mineral phase of bone.[9]

A number of mechanisms have been proposed to explain the bioactive behaviour of glasses and glass-ceramics. The most widely accepted mechanisms are associated with the researchers Hench and coworkers,[10–13] Kokubo and coworkers,[14–17] Andersson and coworkers[18–20] and Li and coworkers.[21–24] Rather than distinct, these different mechanisms give additional explanations for specific details concerning the apatite layer formation.

Due to ethic constrains related to the performing of in vivo tests, an extensive appeal to in vitro tests, either in cellular or in acellular medium, has been made, aiming to understand the bioactive behaviour of materials. Factors such as chemical composition, surface topography and glass structure are believed to play an important role in the surface interaction of glasses and glass-ceramics with the surrounding medium.[25–27]

Most of the typical compositions of glasses and glass-ceramics for biomedical applications belong to quite complex systems. Thus, the understanding of the individual function of each component in the system is not always straightforward, although new advances are occurring due to the most recent sophisticated experimental techniques.

The importance for bioactivity of the presence of Si and P in the glass composition has been widely discussed.[20,28,29] The effect of particular oxides, such as Na_2O,[30,31] MgO,[30] B_2O_3,[30,31] Al_2O_3,[30–32] Fe_2O_3[33] and F^-[30,31] on the surface reactivity of glasses has also been studied, mostly for the SiO_2–CaO system, although references to other systems are also found in the literature.[34,35]

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The role of MgO on the surface behaviour of bioglasses has led to contradictory explanations, in part because it appears in the glass structure either as a modifier or as a network former. Some in vitro results indicate that MgO inhibits mineralization[30,36] and others suggest that it does not affect the apatite formation.[37] However, significant amounts of MgO are present in some Bioverit glass-ceramics, whose bioactivity has been clinically confirmed for years.[38,39] Most recent investigations on the SiO_2–CaO–MgO–P_2O_5 system, by one of the authors of the present paper, also showed that high MgO contents can promote in vitro apatite formation.[40]

This study has been extended to other MgO-rich compositions in the same system and the present work reports the behaviour in a simulated body fluid of two of those glass compositions. The formation of a Ca–P rich layer on the surface of both glasses has been discussed in terms of its composition and the observed results have been explained on the basis of the ionic concentration and pH changes in the immersion liquid. In agreement with the previous findings, it is shown that the high MgO content of both glass compositions does not hinder their apatite-forming ability.

2. Materials and methods

Two glass compositions of the MgO–CaO–P_2O_5–SiO_2 system (Table 1) were prepared from batch mixtures of reagent grade $Ca(H_2PO_4)_2$, $CaCO_3$, MgO and SiO_2. These compositions were chosen among several batches prepared from a line of constant SiO_2/MgO = 55/45 (wt.%) in the equilibrium diagram represented in Fig. 1, and correspond to the higher MgO contents tested. These compositions are identified in Table 1 by Mg31 and Mg36, where the numbers refer to the approximate MgO molar percent in the glass.

Table 1
Investigated glass compositions (mol%)

Sample	SiO_2 (%)	CaO (%)	P_2O_5 (%)	MgO (%)
Mg31	25.37	32.62	10.87	31.14
Mg36	29.37	25.96	8.65	36.02

The raw materials were mixed in ethanol for 45 min and dried at 60 °C during 24 h.

Batches of 80 g were melted in a platinum crucible in air at 1500 °C for 1 h, and then quenched in water in order to produce a glass frit.

The glass frit was melted again at 1500 °C for 2 h and poured onto a brass mold. The obtained block was annealed for 30 min at 730 °C, a temperature previously indicated by Differential Thermal Analysis (DTA) as being close to T_g of both glasses, and then slowly cooled to room temperature. To confirm the amorphous state of the samples, a portion of the obtained block was crushed and taken for powder X-ray diffraction (XRD) using Cu Kα radiation.

For the in vitro tests the parent glass block was cut with a low-speed diamond disc to prismatic specimens of 10 mm × 10 mm × 1 mm. These samples were polished with sandpaper, alumina powder and washed sequentially with water and acetone for 15 min in an ultrasonic cleaner.

In vitro immersion tests were carried out, without stirring, in polyethylene containers where the samples were soaked for different times (1, 2, 5, 7, 14, 21 and 30 days) in 10 ml of a Kokubo's simulated body fluid (SBF), with the composition shown in Table 2. This solution was buffered at pH 7.4 with 50 mM tris(hydroxymethyl)aminomethane and 45 mM hydrochloric acid. The flasks with the solution and the

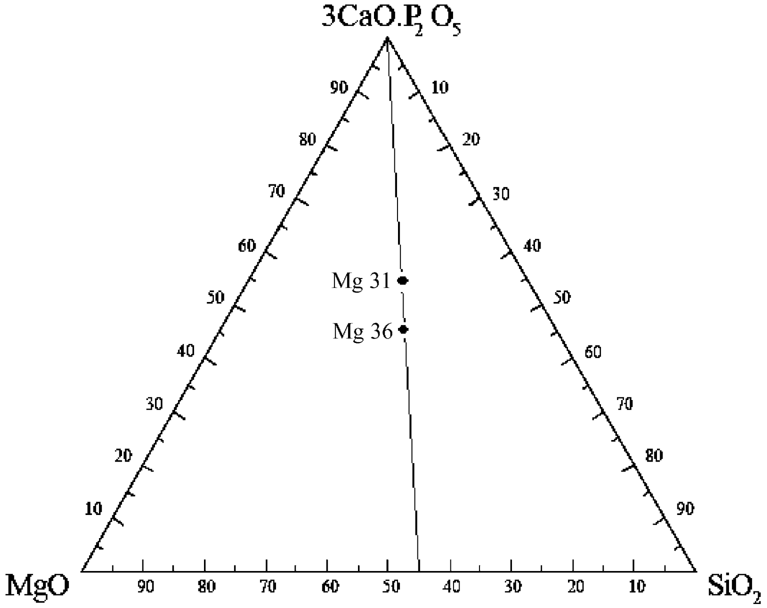


Fig. 1. Phase diagram of the $3CaO{\cdot}P_2O_5$–MgO–SiO_2 system with indication of compositions Mg31 and Mg36 on the line SiO_2/MgO = 55/45 (wt.%).

Table 2
Ion concentration ($mol\,l^{-1}$) of Kokubo's Simulated Body Fluid (SBF) and human blood plasma

	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	$HCO_3{}^-$	$HPO_4{}^{2-}$	$SO_4{}^{2-}$
Plasma	142.0	5.0	2.5	1.5	103.0	27.0	1.0	0.5
SBF	142.0	5.0	2.5	1.5	147.8	4.2	1.0	0.5

specimens were kept at 37 °C during the immersion experiments. Aliquots of solution (2 ml) were taken at the same test times from the containers to measure the ionic concentrations of Ca, P, Si and Mg by induced coupled plasma (ICP) emission spectroscopy using a Jobin-Yvon JY70 Plus spectrometer. The pH of the solution was recorded along the immersion tests.

Surface modifications of the materials were studied by scanning electron microscopy (SEM) on a Hitachi S-4100 with associated energy dispersive spectroscopy (EDS). Specimens were then removed from the SBF after the test times, washed with acetone, dried and set up in a sample holder. All specimens were carbon covered before observation in SEM.

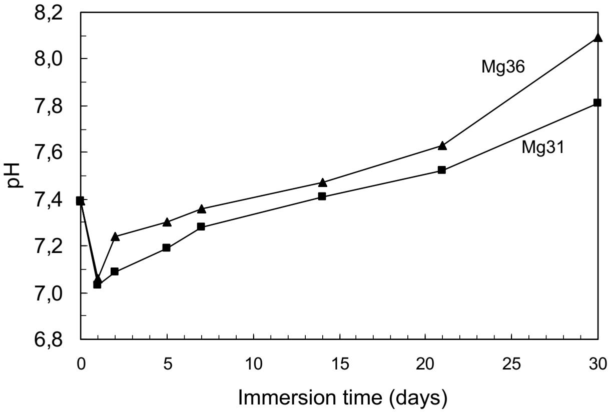


Fig. 3. Time dependence of SBF pH with immersion of glasses Mg31 (■) and Mg36 (▲).

3. Results and discussion

Both Mg31 and Mg36 showed to be amorphous materials, as confirmed by X-ray diffractograms in Fig. 2.

Soaking of these glasses in SBF causes the change in pH represented in Fig. 3. In both cases a considerable acidification of the solution is produced as soon as immersion of the glass samples takes place. The pH values increase again after the first day of incubation, the initial values being recovered between the first and the second week. At the end of the first month the pH of the solution containing Mg31 increased about 6% and the pH of Mg36 solution became 9% higher.

SEM micrographs of the specimens after different soaking times (Figs. 4a–g and 5a–g) clearly show the formation of a layer precipitating on the glass surface, which should be associated to the observed pH changes. Evident signs of detaching of the layers from both glasses are observed, soon after 1 day of immersion (Figs. 4a–c and 5a–c).

Micrographs in Figs. 4d, g and 5d, f, g show that, after about 1 week, consecutive layers precipitate on the glass surface; as a freshly formed layer detach from the glass, a new one immediately starts to build up below it, covering the base glass (see Fig. 5f).

EDS measurements in SEM performed in Mg31 and Mg36 specimens, at the surface of the precipitated layer and on the uncovered glass indicated that the composition of the precipitated layers is rich in Ca and P, when compared with the composition of the original glasses. These results appear quite intelligible in Figs. 6a and b, where the atomic

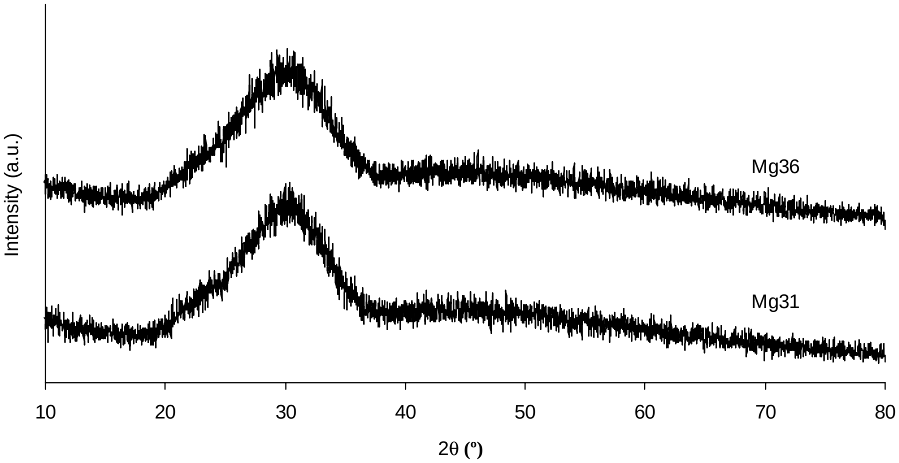


Fig. 2. XRD patterns of glasses Mg31 and Mg36.

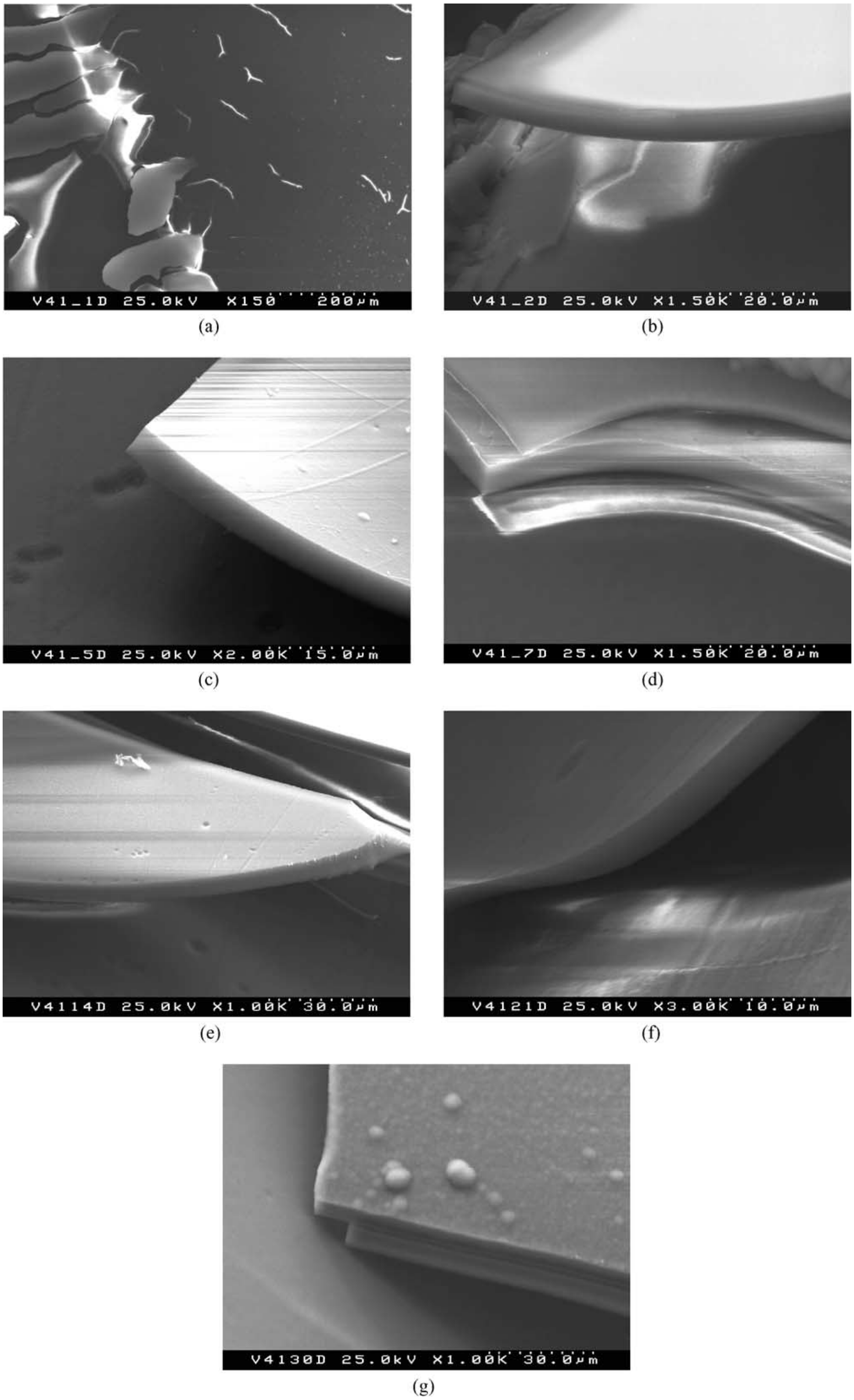


Fig. 4. SEM micrographs of Mg31 samples after soaking in SBF for: (a) 1 day; (b) 2 days; (c) 5 days; (d) 7 days; (e) 14 days; (f) 21 days; (g) 30 days.

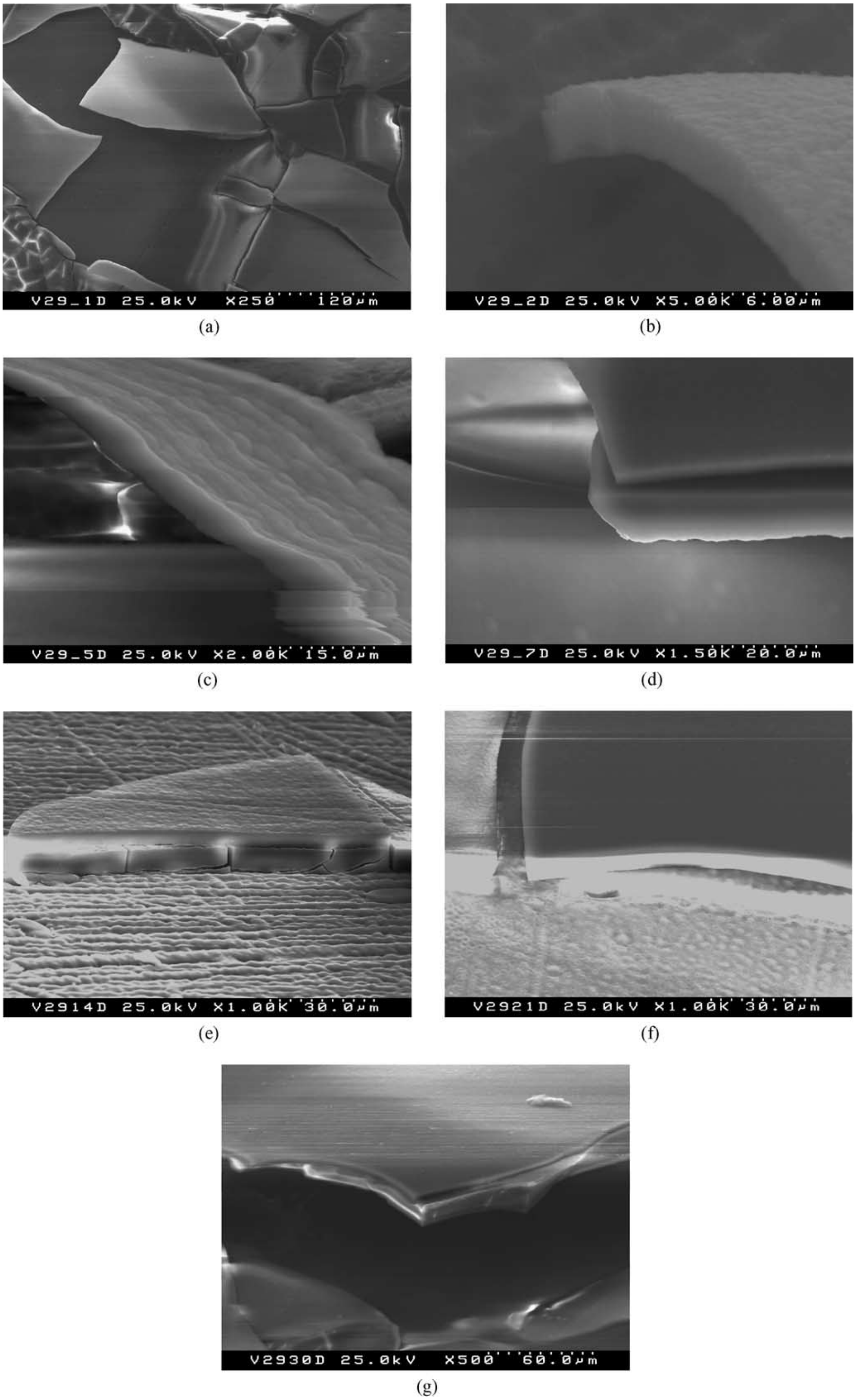


Fig. 5. SEM micrographs of Mg36 samples after soaking in SBF for: (a) 1 day; (b) 2 days; (c) 5 days; (d) 7 days; (e) 14 days; (f) 21 days; (g) 30 days.

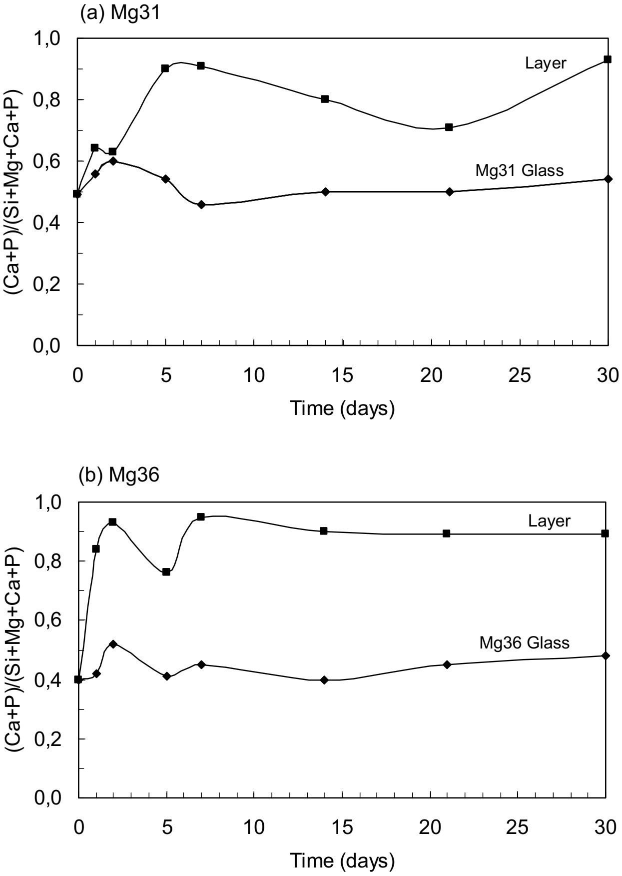


Fig. 6. Variation with immersion time in SBF of the atomic ratio $(Ca + P)/(Ca + P + Si + Mg)$: (a) at the surface layer and on the uncovered Mg31 glass; (b) at the surface layer and on the uncovered Mg36 glass.

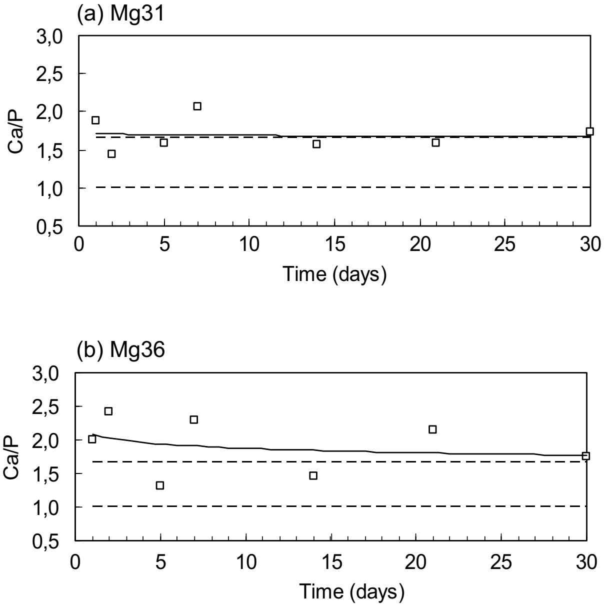


Fig. 7. Ca/P atomic ratio at the layers precipitated (a) on Mg31 glass (b) on Mg36 glass. (Dashed lines indicate the limits $Ca/P = 1$ for brushite, $Ca(HPO_4)2(H_2O)$, and $Ca/P = 1.67$ for hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$.)

ratio $(Ca + P)/(Ca + P + Si + Mg)$ in the surface layer and in the uncovered glass is represented as a function of the immersion time.

The above data undoubtedly show that the layer precipitated on the surface of both compositions is a calcium-phosphate film. The average Ca/P atomic ratio is around 1.5 in the layer covering Mg31 and ranges from 2.5 to 1.5 in the layer covering Mg36, as shown in Fig. 7a and b.

In stoichiometric hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, the Ca/P atomic ratio is 1.67, a value usually reported for natural bones.[41] However, lower values can be found in Ca–P layers when hydroxyapatite is carbonated or when there is precipitation of other stable calcium–phosphate phases,[41] such as brushite, $Ca(HPO_4)2(H_2O)$, where $Ca/P = 1$. This crystal sometimes precedes the formation of hydroxyapatite.

Due to the particular features of both deposits in the present study, it was not possible to determine whether the Ca–P layers were amorphous or crystalline.

The observation of the micrographs in Figs. 4 and 5 can give a rough indication of the film growing rate, by monitoring the evolution of the thickness of layers with soaking time, without accounting for the detaching of individual layers from the substrate glass. This is shown in Fig. 8, where the layer thickness for the longer times was measured on the micrographs by summing up the thicknesses of the different superposed layers.

Immersion of the materials in SBF causes a strong dissolution of all the ions, Si, Mg, Ca and P, from the glasses. Special attention will be given to Ca and P, since these are most directly involved in the formation of the apatite layer. Figs. 9a and b represents the evolution with time of the elemental concentrations of Ca, P and Si in the synthetic fluid for both materials. Either for Mg31 or for Mg36 an intense leaching of Ca and P is observed during the first 1–2 days of incubation, followed by a significant consumption of these ions from the solution, clearly evident until the fifth day. It is also seen that Si is continuously dissolving from the glass. The fall in Ca and P concentrations in the solution, starting at the first day for Mg31 and at the second day for Mg36, leads to a higher relative increase in the amount of Si in the

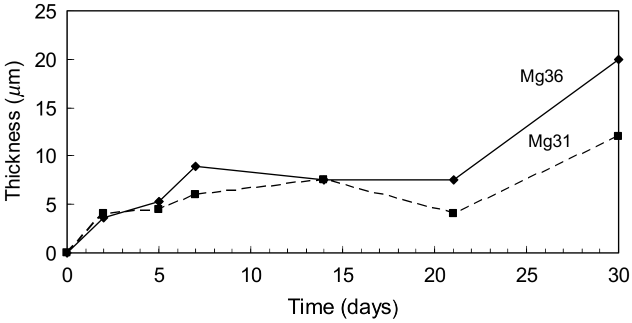
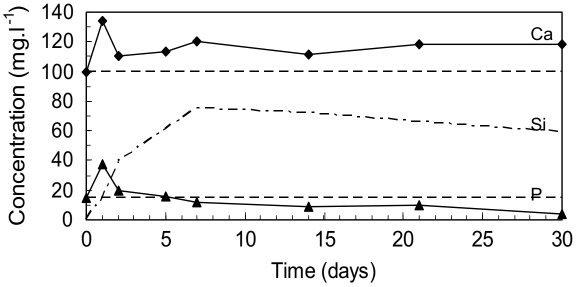


Fig. 8. Thickness of Ca–P layers precipitated on glasses Mg31 and Mg36.

(a) Mg31



(b) Mg36

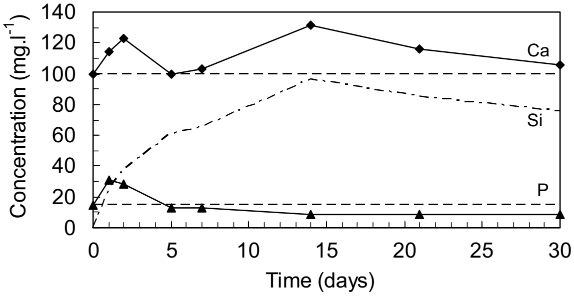


Fig. 9. Ca, P, and Si concentrations by ICP of SBF after immersion of (a) Mg31 and (b) Mg36. (Dashed lines refer to Ca and P concentrations in the virgin SBF.)

solution. These facts, promoting a gradual acidification of the fluid, can explain the decrease of pH values at short times (Fig. 3). A similar acidification phenomenon, due to excess of silica, is well known in the glass industry. It usually takes place at the end of the glass melting reactions, during the digestion of the residual batch silica.[42]

Fig. 9 also shows that along the whole immersion time Ca concentration keeps higher than its initial value in the virgin solution, represented by the upper dashed line. The same behaviour is found for P up to 5 days incubation, after which the concentration in the solution slightly decays when compared with its value for zero time, represented by the lower dashed line.

SEM micrographs and EDS analysis clearly showed that the layers on the glass surfaces are apatite-like precipitates, being Ca and P obviously provided by the solution. Since up to about 5 days both Ca and P concentrations in the solution keep higher than the values for zero time, it becomes evident that the build up of the apatite film during the first 5 days results from these ions coming from the glass samples, severely attacked by the fluid, and then reprecipitated on the glass surface.

P concentration values decrease below the reference for the virgin solution only after 5 days incubation. A simple exercise combining informations from Figs. 7 and 9 indicates that, to obtain Ca–P films with the Ca/P ratios shown in Fig. 7, from Ca and P in the solution, there is no need to consume the amounts of P suggested by the trends in Fig. 9, but much less than that. This means that, if P is being consumed from the solution and if no other phosphate-based compound was detected as a precipitate on the glass surface, then a different P-compound has quite probably formed somewhere, inside the fluid container.

The results of the present work have shown that high MgO contents in the glass compositions do not inhibit their apatite-forming ability. The obtained Ca–P films were not satisfactorily attached to the substrate glass, but nothing seems to indicate that such fact should be directly attributed to the presence of Mg. Experimental evidences in a previous work with compositions of the same system[43] strongly support the idea that glass-ceramics, rather than glasses, promote a better adhesion of the film to the base material. Additional processing work with the glasses of the present study is under way, namely the performing of controlled thermal treatments, aiming the production of glass-ceramics with appropriate crystalline phases and adequate surface topography for the anchorage of the Ca–P layer.

The feeble bonding of the Ca–P layer to the base glasses represents a drawback to their application as monolithic bodies. However, following a procedure adopted for other glasses, the powdering of these glasses and their use as polymeric-based composite fillers is highly promising.[44] In most of these composites the polymer is non-bioactive and the glass furnishes the initiator sites for the apatite deposition on the surface composite.

Another well known effect of the presence of Mg during the precipitation of the apatite films is its tendency to induce the formation of amorphous structures, rather than crystalline precipitates [45–47]

A great discussion on the effects of Mg on mineralization is still running. The most recent developments on the interpretation of surface reactivity of bioglasses suggest that it is not the composition of the glass by itself, but the structural arrangement of the ions within the glass network, that governs the type of interaction with the surroundings, either in in vitro or in in vivo situations.[28,40,48,49]

4. Conclusion

Two silica–calcium–phosphate glasses with high MgO content have shown apatite-forming ability after immersion in a simulated body fluid. These apatite layers, with Ca/P atomic ratios tending to 1.5 with increasing immersion times, were mainly built up from Ca and P dissolved from the glasses and then reprecipitated on their surfaces. Both films were loosely bound to the base glasses, a situation not convenient if the glasses are to be used as monolithic bodies. Powdering of these glasses to use as polymer-based composite fillers is under study and it seems highly recommended.

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