Original Article

Kinetics of conversion of brushite coatings to hydroxyapatite in alkaline solution

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\textbf{A B S T R A C T}

This work describes the kinetics of conversion of brushite coatings, produced by chemical deposition, to hydroxyapatite. The conversion was performed in alkaline solution at three temperatures: 50 °C, 55 °C, and 60 °C. The evolution of the transformation was assessed by X-ray diffraction, and the phase fractions were determined by Rietveld refinement. The Johnson–Mehl–Avrami equation was applied to the data in order to describe the conversion mechanisms. The value of 42 kJ/mol obtained for the conversion activation energy is of the same order as found in similar surface-controlled dissolution processes. The Avrami exponent was $n = 3.5$, which is consistent with an interface-controlled growth of three-dimensional HA crystals with decreasing nucleation rate.

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1. Introduction

Osseointegration is the main requirement for the surgical success of dental implants. For this reason, numerous studies have been conducted in order to increase the bioactivity and osseoconductivity on implant surfaces. For example, morphological changes on titanium (Ti) implant surfaces, from machined to rough/porous surfaces, enhance bone deposition and provide higher primary stability [1]. Additionally, physicochemical modifications on titanium surface may alter the characteristic of this bioinert implant, from passive to bioactive, making it able to biologically instructing the environment for bone tissue repair at atomic level [2]. Following this concept, there is a growing effort toward the production of an ideal biomaterial surface that induces the protein adsorption process and activates specific cellular responses for overcoming the current therapy. Among innumerable applications, calcium phosphate (CaP) coatings, such as $\text{Ca}_{10}(\text{PO}_{4})_6(\text{OH})_2$ (hydroxyapatite), have been extensively investigated as a biomaterial for titanium dental implants due to its chemical similarity to the inorganic phase of bone [2].
It is well-known that CaP precipitation in aqueous media is driven by solution supersaturation, which is achieved by increasing the Ca\(^{2+}\) and PO\(_{4}^{3-}\) ions concentration and/or solution pH [3]. Moreover, the solution temperature may also contribute to supersaturation, because solubility of Ca\(^{2+}\) and PO\(_{4}^{3-}\) ions decreases as temperature increases [3]. Although supersaturation is a necessary condition for precipitation, it is not sufficient. Besides the thermodynamic driving force, nucleation and growth depend on temperature in order to overcome the activation barrier of the process. Therefore, the sequence of CaP precipitation from a supersaturated solution is regulated by both thermodynamic solubility product and kinetic factors; eventually, the first metastable precipitate may undergo changes to a most stable one. Brushite (CaHPO\(_{4}\).2H\(_{2}\)O) has been reported as the stable phase in acidic environments, whereas metastable phases, such as amorphous calcium phosphate (ACP), octacalcium phosphate (OCP), monetite (CaHPO\(_{4}\)), and even brushite, act as precursors of hydroxyapatite (HA) in alkali conditions [4].

The formation of HA from CaP compounds in aqueous media has been reported as a dissolution–precipitation process [3–5], occasionally by “local solution chemistry” [5]. Furthermore, the dissolution rate of the parent phase is enhanced by nucleation and growth of the new phase [5]. There are several studies on chemical and hydrothermal transformations that promotes HA formation, e.g., the two-step chemical deposition that leads to a full conversion of monetite precursor crystals to HA by immersion in alkaline solutions at 60°C [6,7]. However, the conversion kinetics, which can describe the HA nucleation and growth mechanisms, is hardly explored in the literature.

Phase transformations involving nucleation and growth can be studied by the empirical Johnson–Mehl–Avrami (JMA) equation, which describes the isothermal kinetics of a wide variety of transformations in metals [8,9]. The main advantage of using a kinetic approach in a phase transformation study is that the resulting empirical parameters may provide a description of the active mechanisms in the transformation. The present study investigates the kinetics of conversion of brushite coatings, produced by chemical deposition, to HA. The transformation kinetics was studied at different temperatures and times in order to understand the nucleation and growth mechanisms that are present in the conversion.

2. Materials and method

2.1. Deposition of CaP coatings and conversion to HA

Calcium phosphate coatings were deposited on titanium substrates (Ti/CaP) by the two-step chemical deposition method [7]. The two-step route was chosen as it provides layers with better adhesion to the substrate. Experimental details are described elsewhere [10]. Briefly, the cylinder shaped substrates (8.0 mm length, 3.8 mm diameter) were ground on a 600 grade SiC paper and ultrasonically cleaned for 10 min in the following baths: ultrapure water, acetone, ultrapure water, ethanol, and ultrapure water. Then, a precursor solution was prepared under magnetic stirring as follow: firstly, 250 ml of a 1 M lactic acid solution (C\(_{3}\)H\(_{6}\)O\(_{3}\) – VETEC) were added to 250 ml of a 0.5 M calcium hydroxide solution (Ca(OH)\(_{2}\) – MERCK) and kept at room temperature under magnetic stirring; after 30 min, 250 ml of 0.3 M phosphoric acid (H\(_{3}\)PO\(_{4}\) – MERCK) were slowly added to the previously prepared solution at a rate of 8 ml/min. After the addition of the phosphoric acid, the solution presented a translucent appearance and pH below 4. The Ti substrates were then immersed in the solution and the deposition was carried out at 70°C, for 6 h, after which the substrates were completely coated. The thickness of the layers was roughly 20 μm.

After coating the Ti substrates, the Ti/CaP samples were submitted to a chemical treatment in alkaline solution in order to foster the conversion of CaP coatings to HA. The conversion step was performed in a 0.1 M KOH solution (pH = 12) at three different temperatures: 50°C, 55°C, and 60°C. Reactions carried out above 60°C evolved too fast to be followed; therefore, temperatures below 60°C were chosen in order to investigate the formation of the new phase. For each temperature, a set of Ti/CaP samples was simultaneously immersed in the alkaline solution. Thereafter, each sample was removed from the solution, at different times, in order to produce a set of partially converted Ti/CaP-HA samples.

The samples were characterized by X-ray diffraction (XRD) and scanning electron microscopy with field emission gun before and after conversion. The evolution of HA phase was assessed by XRD, using a PANalytical X’Pert X-ray diffraction equipment, with CuKα radiation, at 40 kV and 40 mA. The 2θ scanning ranged from 10° to 80°, with a step-size of 0.02°, at 100 s/step. Rietveld refinement method was applied to the diffractograms, in order to determine the percentages of each phase [11]. The refinement was performed using the TOPAS Academic software, version 4.1, which includes First Principals (FP) calculations [12] for phase determination. For these calculations, the following parameters were adjusted: lattice parameter, crystallite size, and scale, the value of the latter one indicating the weight percentage. The parameters for the proposed hydroxyapatite (ICSD card 34457) were: (i) space group: P1121/b; and (ii) lattice parameters: a = 9.4214 Å; b = 18.8428 Å; c = 6.8814 Å. Scanning electron microscopy (SEM) analyses were performed in a FEI Quanta 250FG microscope with field emission gun (FEG), operating on both high and low vacuum modes, between 1 and 30 kV. Prior to the morphological analyses, the samples were coated with a thin platinum layer in order to avoid electrical charging while maintaining the nanometric features of the surface.

2.2. Kinetic study background

The active mechanisms in the conversion of brushite coatings to HA were investigated using the Avrami theory of nucleation and growth [8,9]. The main result of this model is the Johnson–Mehl–Avrami (JMA) equation (Eq. (1)), which gives the volume fraction of the new phase (q) as a function of the time (t). This equation is exact over the whole range of volume fraction, provided the precipitate of new phase grows three-dimensionally and linearly with time. However, Eq. (1) can be used to indistinctly describe other growth mechanisms in the early stages of transformation, when the effects of nuclei impingement and preferable nucleation sites are negligible [9].

In Eq. (1), k is the temperature-dependent rate constant, which
is related to the activation barrier of the transformation and \( n \) is the Avrami exponent, which provides information about the nucleation and growth mechanisms of the new phase. These parameters can be determined by fitting Eq. (1) to the isothermal transformation curves. The activation barrier (\( E_a \)) can be determined by plotting the time required for a specific transformed fraction, \( t_v \), as a function of the reciprocal of the temperature [9], as shown in the Arrhenius equation (Eq. (2)). The time \( t_v \) is directly obtained from the isothermal curves.

\[
y = 1 - \exp\left(-kt^n\right) \\
\ln t_v = \ln t_0 + \frac{E_a}{RT}
\]

(1)

(2)

The time exponent, \( n \), is related to the nucleation rate and type (interface or diffusion-controlled) and dimension of growth. For example, \( n \) is found to be 3 for a fixed number of nuclei (i.e., zero nucleation rate) growing three-dimensionally and linearly with time (interface controlled). In this case, the value of \( n \) is 3 because, according to the model, \( y = 1 - e^{-Vt} \), where \( V \) is the volume of the spherical nuclei of radius \( r \), given as \( 4/3\pi r^3 \) [9]. In analog way, \( n \) is found to be 3/2 when these nuclei grow proportional to the square root of the time (diffusion controlled). For a non-zero nucleation rate given by \( N = ct^b \) (\( c \) and \( b \) are constants), the contribution of the nucleation can be included in the Avrami exponent by adding \( (b + 1) \) to the abovementioned values of \( n \), which are associated to growth without nucleation.

3. Results and discussion

3.1. Conversion of CaP coatings to HA

Fig. 1 shows the X-ray diffractograms of the as-deposited Ti/CaP sample and titanium substrate (JCPDS card #01-089-2959). The untransformed CaP is composed of a single crystalline phase, brushite, according to the JCPDS card #01-089-0377. For the sake of clarity, only the most intense brushite peaks were labeled. Non-brushite peaks in the as-deposited CaP diffractogram are due to the titanium substrate. The precipitation of brushite, rather than other CaP phases, was compatible with the acidic medium of the precursor solution [3]. Monetite, the non-hydrated form of brushite, did not precipitate in these conditions probably due to the low temperature (70 °C), which favored the lower surface energy hydrated structure [3,4].

Fig. 2 shows the XRD patterns of Ti/brushite samples transformed at 50°C, 55°C and 60°C. The evolution of the brushite/HA conversion is clearly seen. There is a decrease of the brushite peaks, e.g. (002) and (021), at 11.7° and 20.9°, respectively, and a progressive increase on the HA peaks (JCPDS card #01-089-4405), e.g. the most intense ones, at 25.8° and 32.2°, as a function of the conversion time. The diffraction pattern of the completely transformed sample (Fig. 3) shows the newly formed HA phase, with low/medium crystallinity. The patterns can be assigned to the monoclinic structure of hydroxyapatite, with lattice parameters \( a = 9.495 \) Å, \( b = 18.753 \) Å, and \( c = 6.881 \) Å, as given by the Rietveld analysis. These values are quite close to the ones reported in the literature [13]. Ti-substrate peaks can also be seen. The presence of Ti peaks confirms that X-rays are always reaching the substrate, and then the brushite parent phase. Intermediate phases were not found, except at 60°C (Fig. 2c), where a small fraction of monetite (maximum 2.11%) was formed. The presence of monetite was not expected in this experimental condition (\( pH = 12 \)) and possibly occurred by the dehydration of the brushite structure at the highest temperature. In fact, in situ studies on brushite-HA conversion have shown the presence of monetite as an intermediate phase and a two-phase HA-monetite product only at \( pH = 6.5 \). At higher \( pH \) values, intermediate phases have not been reported [14].

Tables 1–3 show the phase percentages of brushite, monetite, and HA obtained by the Rietveld refinement of the diffractograms at different times and temperatures. The titanium fraction coming from the substrate was also included. For all the Rietveld calculations, the weighted-profile R factor (Rwp) and Goodness of Fit (GoF) values ranged from 11 to 17 and from 1.1 to 1.9, respectively, indicating that the fitting was quite acceptable. It should be noted that there is a time required for starting the transformation to HA, and that this time decreases when the temperature is increased. The existence of this period of time, or incubation time, at each temperature can be seen in Fig. 4, which shows the HA transformed fraction (y) as a function of time (the HA fraction was calculated as the ratio between %HA and %HA+%brushite+%monetite). The sigmoidal shape of the transformation curves and the existence of an incubation time strongly suggest that the formation of HA occurs via nucleation and growth process. Also, the fact that the increase in the conversion temperature leads to higher transformation rates is in accordance to the thermally activated nature of the reaction.

The activation barrier for the brushite-HA conversion was determined from the Arrhenius plot shown in Fig. 5. The obtained value of \( E_a \) was \((42 \pm 3) \) kJ/mol, much smaller than those reported for the homogenous precipitation of HA in aqueous medium, which are roughly 180 kJ/mol [15,16]. This difference was expected since our conversion process is essentially heterogeneous, then requiring a smaller activation energy. This \( E_a \) value should then be better compared to the
Fig. 2 – XRD patterns of Ti/brushite samples converted to hydroxyapatite in the presence of alkaline solution at 50 °C, 55 °C, and 60 °C, for different times.

Fig. 3 – XRD patterns of hydroxyapatite obtained from a Ti/brushite sample treated in the presence of alkaline solution at 50 °C, for 180 min.

**Table 1 – Phase quantification in Ti/brushite samples converted to HA at 50 °C.**

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>HA (%)</th>
<th>Brushite (%)</th>
<th>Monetite (%)</th>
<th>Titanium (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>97.15</td>
<td>0</td>
<td>2.85</td>
</tr>
<tr>
<td>25</td>
<td>0</td>
<td>99.56</td>
<td>0</td>
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<td>50</td>
<td>13.81</td>
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<td>0</td>
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<td>70</td>
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<td>0</td>
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</tr>
<tr>
<td>85</td>
<td>64.23</td>
<td>34.87</td>
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</tr>
<tr>
<td>105</td>
<td>66.17</td>
<td>33.82</td>
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<td>120</td>
<td>77.50</td>
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<td>180</td>
<td>98.04</td>
<td>0</td>
<td>0</td>
<td>1.96</td>
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</tbody>
</table>

**Table 2 – Phase quantification in Ti/brushite samples converted to HA at 55 °C.**

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>HA (%)</th>
<th>Brushite (%)</th>
<th>Monetite (%)</th>
<th>Titanium (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>97.38</td>
<td>0</td>
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<td>30</td>
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<td>77.67</td>
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<td>105</td>
<td>86.00</td>
<td>8.76</td>
<td>0</td>
<td>5.24</td>
</tr>
</tbody>
</table>

**Table 3 – Phase quantification in Ti/brushite samples converted to HA at 60 °C.**

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>HA (%)</th>
<th>Brushite (%)</th>
<th>Monetite (%)</th>
<th>Titanium (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>97.15</td>
<td>0</td>
<td>2.85</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>97.45</td>
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<td>2.55</td>
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<td>20</td>
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<td>81.86</td>
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<td>1.52</td>
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<td>84.11</td>
<td>7.03</td>
<td>2.11</td>
<td>6.75</td>
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ones reported for heterogeneous processes. For example, it has been suggested that the dissolution of brushite in pseudo-physiological solutions occurs via diffusion of ions through the volume and surface, both mechanisms playing an important role in the dissolution rate [17]. The dominance of the surface mechanism – desorption and diffusion of molecules/ions on the brushite surface – has been reported for low stirring and high pH conditions [17,18]. The surface-controlled dissolution process was also proposed by Kanzaki et al. [19] and Onuma et al. [20], when monitoring brushite crystal planes under pseudophysiological solutions. They found that the two stages of the surface mechanism – detachment and diffusion of molecules – had similar contributions to the dissolution rate, and that the activation energy was in the range of 36–43 kJ/mol. Therefore, the value of the 42 kJ/mol determined in this work, which includes the activation barrier for both, dissolution and precipitation, suggests that the conversion of brushite coatings to HA in alkaline media is a dissolution-controlled process.

3.2. Morphological changes

It is well-known that brushite and HA crystals exhibit distinct morphologies [21]. Therefore, morphological changes were followed by SEM analyses in order to have a deeper understanding of the conversion mechanism.

Fig. 6 shows FEG-SEM micrographs of untransformed and partially transformed Ti/brushite samples. The thin plate-like morphology of brushite crystals exhibited by the as-deposited Ti/brushite sample (Fig. 6a) has also been reported by other authors [22]. Fig. 6b shows the surface morphology of a Ti/brushite sample treated in alkaline solution at 60 °C, for 10 min. This conversion time, as shown in Fig. 4, is within the incubation range, i.e., the HA phase is not present yet. One can observe that the conversion treatment did not cause either macro- or micromorphology changes, but it brought about severe nanometric surface modifications on the brushite crystals. These changes indicate a local dissolution process, which led to the formation of pits and surface roughness. This obser-

vation is in accordance to in situ studies on the dissolution of the (010) brushite plane, with HA precipitation just after brushite dissolution [19]. The surface morphology of a partially transformed Ti/brushite sample is shown in Figs. 6c (front view) and 6d (cross-section view), for the sample converted in alkaline solution at 50 °C, for 70 min (40% of HA, as given by Rietveld analysis). One can observe the brushite crystals acting as substrates for the HA heterogeneous nucleation. A three-dimensional nanometric precipitation is seen all over the crystal surface. The transversal view of this sample, shown in Fig. 6d, shows the HA phase on the brushite crystal surface, as well as into the brushite crystal, suggesting that HA grows from the surface to the core of the brushite crystal. The converted samples with more than 75% HA exhibited a predominance of HA, not only on the surface but also inside the volume of brushite crystals.

Fig. 7 shows the morphology of samples completely converted to HA, at 50 °C, for 3 h, 12 h, and 24 h. A preservation of macro- and micromorphology of the precursor crystals was observed, however, with the presence of three-dimensional nano-HA crystals. It can also be verified that the HA crystals grow according to the time. The nano needle-like morphology is characteristic of HA converted at low temperatures and was also observed in previous studies [10,23,24]. This morphology contributes to an increase of the surface area when compared to the precursor phase, and can be considered an advantage, as better clinical outcomes in implantology have been associated to nanostructured surfaces [25]. In the sample converted for 24 h, a time much higher than that required to 100% transformation into HA, it can be seen that the needle-like morphology is kept and that the nanosized crystals grew with the formation of a highly oriented structure. These results are in accordance to those reported by Zou et al. [26], that suggested an epitaxial growth of HA crystals due to the similarity of crystal- line structure between brushite and HA. The HA coating produced by the chemical deposition method exhibited HA crystals with thickness below 100 nm, which is comparable to the crystallite size of the apatite found in the mineral phase of bone [27].
These morphological analyses confirm that the brushite-HA conversion occurs by surface dissolution of brushite followed by nucleation and growth of three-dimensional HA nanocrystals. It is possible that the formation of pits on the brushite surface (Fig. 6b) and the gaps between the HA crystals (Fig. 7a), contribute to the transference of Ca²⁺ and PO₄³⁻ ions from the solution to the core of the brushite crystals, supporting the phase transformation in a process similar to other mineral replacement reactions [5,28].

3.3. Application of the Avrami theory

Although JMA equation has been mostly used to describe the isothermal kinetics of reactions in metal systems, it is worth to analyze the kinetic data of Fig. 4 in the light of this theory. Fig. 8 shows the Avrami linear plot (Eq. (1)) of the experimental data (only the lowest values of the transformed fraction were considered as they represent phenomena acting in the early stages of transformation, when the effects of nuclei impingement are not present yet). The Avrami’s exponent $n$ was obtained from the tangent of the curves. The values of $n$ are $3.7 \pm 0.1$, $3.7 \pm 0.1$ and $3.1 \pm 0.6$, respectively for the 50°C, 55°C, and 60°C isotherms. It is interesting to point that the curves have almost the same value of $n$, roughly $3.5 \pm 0.2$ (mean value), as should be expected for a reaction guided by Avrami’s theory. This indicates that the mechanisms governing the brushite-HA conversion do not change in this range of temperature. The value of 3.5 for the Avrami exponent is consistent with a decreasing nucleation rate of HA crystals, given by $N = ct^{-0.5}$, as our results strongly indicate an interface-controlled growth of three dimensional HA crystals. Therefore, the value of 0.5 should be added to the Avrami’s exponent associated to a process without nucleation ($n = 3 + 0.5 = 3.5$).

Although it is well-known that dissolution-precipitation is the main mechanism of CaP-HA conversion in aqueous medium, the kinetics approach is hardly reported in the literature. This is the first kinetic study on the brushite-HA conversion in alkaline media. Ivankovic et al. [7] and Kasiotpas et al. [28] also used the Avrami theory to describe the apatite formation, but the process was quite different from ours. In those works, HA was obtained by the immersion of an aragonite precursor (CaCO₃) into a phosphate solution. In both studies, the product of the transformation was a carbonated apatite, containing traces of substituted ions, as strontium.

Fig. 6 – FEG-SEM micrographs of Ti/brushite samples converted to hydroxyapatite in the presence of alkaline solution at the following temperature/time: (a) as-deposited; (b) 60°C, for 10 min (untransformed); (c) 50°C, for 70 min (partially transformed: 40% of HA), longitudinal view; (d) 50°C, for 70 min (partially transformed: 40% of HA), cross-section view.
While Ivankovic et al. [7] obtained $n = 0.5$, suggesting that the growth of apatite was an one-dimensional process controlled by diffusion, Kasioptas et al. [28] observed two distinct mechanisms in two different temperature ranges: one described by a $n$-value of 0.5 and the other by a $n$-value of 0.77. According to the authors, the 0.5 value was indicative of a diffusion controlled process, as proposed by Ivankovic et al. [7], and the 0.77 value was possibly related to an interface controlled reaction, as proposed by the present work. A comparison between these $n$-values (0.5–0.77) and the one obtained in this work (3.5) should be avoided because the precursor sample, solution composition and pH level were completely different. These parameters and the presence of foreign ions produce a non-stoichiometric apatite, then changing the kinetics of CaP transformation.

4. Conclusion

The kinetics of conversion of brushite coatings to hydroxyapatite in alkaline solution was studied. The application of JMA’s equation to the kinetic curves gave an exponent $n = 3.5$, which is consistent with an interface-controlled growth of three-dimensional HA crystals, with a decreasing nucleation rate. This statement was supported by morphological analyses, that showed the presence of three-dimensional HA nanocrystals, and by the value of the activation barrier for brushite-HA conversion, $42\, \text{kJ/mol}$, which strongly suggests that the process is controlled by superficial dissolution of brushite crystals with posterior HA nucleation and growth.

Conflicts of interest

The authors declare no conflicts of interest.
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