



## Characterization of aqueous interactions of copper-doped phosphate-based glasses by vapour sorption



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### ABSTRACT

Owing to their adjustable dissolution properties, phosphate-based glasses (PGs) are promising materials for the controlled release of bioinorganics, such as copper ions. This study describes a vapour sorption method that allowed for the investigation of the kinetics and mechanisms of aqueous interactions of PGs of the formulation  $50\text{P}_2\text{O}_5-30\text{CaO}-(20-x)\text{Na}_2\text{O}-x\text{CuO}$  ( $x = 0, 1, 5$  and  $10$  mol.%). Initial characterization was performed using  $^{31}\text{P}$  magic angle spinning nuclear magnetic resonance and attenuated total reflectance–Fourier transform infrared spectroscopy. Increasing CuO content resulted in chemical shifts of the predominant  $\text{Q}^2$  NMR peak and of the  $(\text{P}-\text{O}-\text{P})_{\text{as}}$  and  $(\text{P}-\text{O}^-)$  Fourier transform infrared absorptions, owing to the higher strength of the  $\text{P}-\text{O}-\text{Cu}$  bond compared to  $\text{P}-\text{O}-\text{Na}$ . Vapour sorption and desorption were gravimetrically measured in PG powders exposed to variable relative humidity (RH). Sorption was negligible below 70% RH and increased exponentially with RH from 70 to 90%, where it exhibited a negative correlation with CuO content. Vapour sorption in 0% and 1% CuO glasses resulted in phosphate chain hydration and hydrolysis, as evidenced by protonated  $\text{Q}^0(1\text{H})$  and  $\text{Q}^1(1\text{H})$  species. Dissolution rates in deionized water showed a linear correlation ( $R^2 > 0.99$ ) with vapour sorption. Furthermore, cation release rates could be predicted based on dissolution rates and PG composition. The release of orthophosphate and short polyphosphate species corroborates the action of hydrolysis and was correlated with pH changes. In conclusion, the agreement between vapour sorption and routine characterization techniques in water demonstrates the potential of this method for the study of PG aqueous reactions.

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### 1. Introduction

Bioactive glasses have been extensively investigated in recent years [1] and their doping with trace elements offers an attractive approach for the stimulation of antibacterial, angiogenic and osteogenic processes [2–5]. Phosphate-based glasses (PGs) offer a particularly wide range of glass formulations compared to their silicate counterparts [6,7]. Copper-containing PGs possess effective antibacterial properties [3,8] and were recently shown to improve endothelial cell survival under reduced nutrient conditions [9].

The structure of PGs is based on a  $\text{P}_2\text{O}_5$  network consisting of  $\text{Q}^3$  species (i.e. phosphate tetrahedra with three bridging oxygen atoms), which is depolymerized through the introduction of metal oxides, resulting in the conversion of  $\text{Q}^3$  to  $\text{Q}^2$ ,  $\text{Q}^1$  and  $\text{Q}^0$  species (previously reviewed in Ref. [10]). Ionic bonds are thereby formed between the non-bridging oxygen atoms and the metal cations [11]. Due to the increase in bond strength with the cation potential

[12–15], cations with higher valence such as  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{3+}$  or  $\text{Ti}^{4+}$ , act as network crosslinkers and generally increase the chemical stability while decreasing the dissolution rate of the glass [8,12,16–18].

Understanding the relationship between glass composition and dissolution properties is essential for tailoring PGs to a desired biological response. Specifically, dissolution kinetics govern pH changes as well as the duration and rate of ion release, which must be confined to a narrow therapeutic concentration range. Aqueous degradation of PGs is initiated by acid/base-catalysed disruption of the ionic bonds between phosphates and metal cations [11]. The phosphate chains are subsequently hydrated, as evidenced by  $\text{Q}^2(\text{H})$  species in  $^1\text{H}-^{31}\text{P}$  cross-polarization nuclear magnetic resonance (NMR) spectra [19] as well as by  $(\text{P})-\text{O}-\text{H}$  vibration modes in Fourier transform infrared (FTIR) spectra [20]. Moreover, hydrolysis of  $\text{P}-\text{O}-\text{P}$  bonds results in cleavage of phosphate chains, as shown by  $\text{Q}^1(\text{H})$  and  $\text{Q}^0(\text{H})$  species (protonated phosphate tetrahedra) [19–22]. Therefore, PGs release not only metal cations but also polyphosphate anions of various lengths [23], which are known to alter cell differentiation and mineralization [24,25].

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PG reactivity with water is commonly determined by ageing in an aqueous medium and has been correlated with surface energies measured by contact angle analysis [16,26]. However, only a few studies have examined the effect of exposing PGs to water vapour. Vapour sorption induces aqueous reactions in PGs without the loss of the hydrated material that occurs during water ageing and therefore allows for the analysis of structural changes [20,21]. Vapour penetration into phosphorus oxynitride glasses has been quantified by hydrogen depth profiling [27]. Moreover, nuclear waste glasses are typically assessed by optical analysis of the resulting corrosion layer [28].

This study describes a rapid and precise gravimetric vapour sorption method which allowed examination of both the kinetics and mechanisms of aqueous interactions of a CuO-doped PG system. Specifically, dynamic vapour sorption (DVS) was applied to monitor mass changes in PGs of the formulation  $50\text{P}_2\text{O}_5-30\text{CaO}-(20-x)\text{Na}_2\text{O}-x\text{CuO}$  (with  $x = 0, 1, 5$  and  $10$  mol.%; originally described in Ref. [8]) exposed to variable relative humidity (RH) between 0 and 90%. Sorption-induced structural changes were analysed using  $^{31}\text{P}$  NMR and FTIR. Finally, vapour sorption findings were compared with dissolution, cation and polyphosphate anion release, as well as pH changes in deionized water.

## 2. Materials and methods

### 2.1. PG production

Four PG formulations (originally developed for antibacterial purposes [8], Table 1) were produced as previously described [9]. Briefly,  $\text{P}_2\text{O}_5$ ,  $\text{CaHPO}_4$ ,  $\text{NaH}_2\text{PO}_4$  and  $\text{CuO}$  precursors (Alpha Aesar) were homogenized at  $1350^\circ\text{C}$  and quench cast into a cylindrical mould. PGs were cut into discs (2.15 mm thick and 10 mm in diameter) or pulverized and sieved to isolate a particle size fraction of 38–44  $\mu\text{m}$ . The specific surface area of this fraction was determined (for the 1% CuO PG,  $n=3$ ) according to the Brunauer–Emmet–Teller nitrogen adsorption method, using a Micromeritics TriStar 3000 instrument. Prior to the measurements, samples were degassed for 3 h under pure nitrogen flow at  $200^\circ\text{C}$ .

### 2.2. DVS measurements

Vapour sorption of PGs was examined using a DVS Intrinsic (Surface Measurement Systems Ltd., UK) measuring mass changes ( $\pm 0.1 \mu\text{g}$ ) under controlled humidity and temperature. Approximately 27 mg of PG powder was placed in an aluminum pan and inserted into a chamber kept at  $37 \pm 0.05^\circ\text{C}$ . Samples were first equilibrated at 0% RH to determine the dry sample mass ( $m_0$ ). For sorption/desorption isotherms, the RH was increased/decreased by successive steps of 5% over the range 0–90%. At each RH value, the relative mass change,  $\delta m = (m - m_0)/m_0$ , was recorded once equilibrium was reached ( $d(\delta m)/dt < 0.002\% \text{min}^{-1}$ ) or after a maximum of 6 h. In a second method, the mass over a period of 24 h was measured at 90% followed by 0% RH.

**Table 1**  
Glass formulations.

Glass code	Components (mol.%)			
	$\text{P}_2\text{O}_5$	CaO	$\text{Na}_2\text{O}$	CuO
0% CuO	50	30	20	0
1% CuO	50	30	19	1
5% CuO	50	30	15	5
10% CuO	50	30	10	10

### 2.3. Glass characterization before and after DVS

The following characterizations were performed on PG powders before and after DVS at 90 and subsequently 0% RH for 24 h each. Fused PG particles after DVS were repulverized using a mortar and pestle (except for morphological characterization).

#### 2.3.1. $^{31}\text{P}$ NMR spectroscopy

$^{31}\text{P}$  magic angle spinning nuclear magnetic resonance (MAS NMR) spectra were obtained on a Varian VNMRS400 spectrometer at a frequency of 161.8 MHz. Samples were placed in 4 mm rotors and spun at 12500 Hz. A  $30^\circ$  pulse was applied every 5 s and typically 128 scans were accumulated. Origin Pro v.8 software (OriginLab) was used for Gaussian peak fitting in the isotropic region of the spectra.

#### 2.3.2. FTIR spectroscopy

A PerkinElmer Spectrum 400 was used in the attenuated total reflection (ATR) mode to record FTIR spectra in the  $650-4000 \text{cm}^{-1}$  wavenumber range at a resolution of  $2 \text{cm}^{-1}$ . Spectra were generated from 64 accumulated scans and normalized to the total surface area under the phosphate-related absorption bands.

#### 2.3.3. Morphological characterization

Samples were placed on a glass slide and observed on an inverted optical microscope. Scanning electron microscope (SEM) images were obtained on a Hitachi S-4700 field-emission SEM using a working distance of 12 mm and an acceleration tension of 2 kV, following sputter-coating with Au/Pd for 3 min.

### 2.4. Determination of glass dissolution in deionized water

#### 2.4.1. Weight loss

PG discs in triplicates were placed in vials containing 10 ml deionized water (DW) at  $37^\circ\text{C}$ . After 2, 6, 24, 72 and 168 h, the discs were removed from the vials, blot-dried and weighed. The height and diameter were measured using a digital caliper to determine the surface area before the discs were returned to fresh DW. pH changes resulting from PG dissolution were measured using an Accumet XL20 pH meter (Fisher Scientific) and the solutions were stored for cation quantification (see Section 2.4.2). The weight loss at time point  $n$ ,  $W_n$ , was calculated by cumulating the weight changes of all previous time segments divided by the average disc surface area,  $A$ :

$$W_n = \sum_{i=1}^n \frac{W_{i-1} - W_i}{(A_{i-1} + A_i)/2} \quad (1)$$

Weight loss values were plotted against time and the dissolution rate (in  $\text{mg mm}^{-2} \text{h}^{-1}$ ) was determined by linear regression through the origin.

#### 2.4.2. Cation release

Sodium, calcium and copper cations, as well as total phosphorus released from PG discs incubated in DW (as described in Section 2.4.1), were quantified using an inductively coupled plasma (ICP) optical emission spectrophotometer (Thermo Jarrell Ash – TRACE SCAN). Then 4% (w/v) nitric acid was added to all samples in order to stabilize copper cations in their higher oxidation state (2+). Standard solutions (also containing 4% nitric acid) were prepared by serially diluting certified standards to 100, 50, 10, 5 and 1 ppm. The data was plotted as cation mass per surface area (determined from disc dimensions) as a function of time and the release rates (in  $\text{ng mm}^{-2} \text{h}^{-1}$ ) were determined by linear regression through the origin.

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