

# **Preparation of orthophosphate glasses in the MgO–CaO–SiO<sub>2</sub>–Nb<sub>2</sub>O<sub>5</sub>–P<sub>2</sub>O<sub>5</sub> system**

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## **Abstract**

**BACKGROUND:** Niobia/magnesia-containing orthophosphate invert glasses were successfully prepared in our earlier work. Orthophosphate groups in the glasses were cross-linked by tetrahedral niobia ( $\text{NbO}_4$ ) and magnesia.

**OBJECTIVE:** The aim of this work is to prepare calcium orthophosphate invert glasses containing magnesia and niobia, incorporating silica, and to evaluate their structures and releasing behaviors.

**METHOD:** The glasses were prepared by melt-quenching, and their structures and ion-releasing behaviors were evaluated.

**RESULTS:**  $^{31}\text{P}$  solid-state nuclear magnetic resonance (NMR) and Raman spectroscopies showed the glasses consist of orthophosphate ( $\text{PO}_4$ ), orthosilicate ( $\text{SiO}_4$ ), and  $\text{NbO}_4$  tetrahedra.  $\text{NbO}_4$  and  $\text{MgO}$  in the glasses act as network formers. By incorporating  $\text{SiO}_2$  into the glasses, the chemical durability of the glasses was slightly improved. The glasses reheated at  $800^\circ\text{C}$  formed the orthophosphate crystalline phases, such as  $\beta\text{-Ca}_3(\text{PO}_4)_2$ ,  $\text{Mg}_3(\text{PO}_4)_2$  and  $\text{Mg}_3\text{Ca}_3(\text{PO}_4)_4$  in the glasses. The chemical durability of the crystallized glasses was slightly improved.

**CONCLUSIONS:** Orthosilicate groups and  $\text{NbO}_4$  in the glasses coordinated with each other to form Si-O-Nb bonds. The chemical durability of the glasses was slightly

improved by addition of  $\text{SiO}_2$ , since the field strength of Si is larger than that of Ca or Mg.

### **Keywords**

Biomaterials, Phosphate invert glass, Orthophosphate, Magnesium, Silicate, Niobium

## 1. Introduction

Titania-containing calcium phosphate invert glasses (TiCa-PIGs) and niobium-containing calcium phosphate invert glasses (NbCa-PIGs) are composed of short phosphate groups, such as ortho- and pyrophosphates ( $Q_p^0$  and  $Q_p^1$ ), which cross-link with titania/niobia tetrahedral  $TiO_4/NbO_4$  forming a glass network [1-3]. TiCa-PIGs were successfully coated on a Ti-29Nb-13Ta-4.6Zr (TNTZ) alloy by heat-treatment at 800°C for 1 h [4]. The resulting layer, including  $\beta$ - $Ca_3(PO_4)_2$ ,  $\beta$ - $Ca_2P_2O_7$  and  $TiO_2$  (rutile) crystal phases and residual glassy phases, bonded strongly with TNTZ [5,6]. TiCa-PIGs-coated TNTZ showed good bioactivity *in vivo* [4]. NbCa-PIGs enhanced the differentiation of osteoblast-like cells (*e.g.* alkali phosphatase activity, ALP) with a trace amount of niobate ion dissolved from the glasses (0.04 – 0.06 mM) [7].

In our previous work, the nominal composition of 37.5MgO·37.5CaO·20P<sub>2</sub>O<sub>5</sub>·5Nb<sub>2</sub>O<sub>5</sub> (mol%, denoted by 20P) glass and glass-ceramic were prepared, and their structures and release behaviors were discussed as a fundamental work [8]. When MgO was incorporated into the phosphate invert glasses, it acted as an intermediate oxide [9,10].  $Mg^{2+}$  ions released from the glasses are expected to promote cell adhesion [11], proliferation [12] and differentiation [13]. The phosphate

group of 20P was composed exclusively of  $Q_p^0$ , cross-linked by tetrahedral niobate/niobia ( $\text{NbO}_4$ ) and magnesia [8]. 20P showed three glass transition temperatures, which indicate the coexistence of several network structures [8]. The chemical durability of 20P was comparably lower than that of Ti/NbCa-PIGs containing a large amount of MgO in the glass [2,3,8]. The glass-ceramic of 20P included orthophosphate crystal phases and its chemical durability was improved compared with that of the mother glass [8].

A trace amount of silicate ion has been reported to stimulate osteoblast proliferation [14] and differentiation [15], hence, addition of  $\text{SiO}_2$  to the glasses may enhance bone formation. With the exception of certain special compositions, the formation of bonds (such as a P-O-Si bond) between phosphate and silicate groups in glasses is difficult. In this work, we focused on the coexistence of several glass-networks in 20P. By incorporating  $\text{SiO}_2$  into 20P, the silicate group is expected to enter the niobate/niobia or magnesia network. The aim of this work is, as a fundamental work for designing biomedical materials, to prepare  $\text{SiO}_2$ -containing orthophosphate invert glasses, and to evaluate their structures, crystallization behaviors and ions-releasabilities to Tris buffer solution.

## 2. Materials and methods

$(37.5 - x/2)\text{MgO} \cdot (37.5 - x/2)\text{CaO} \cdot 20\text{P}_2\text{O}_5 \cdot x\text{SiO}_2 \cdot 5\text{Nb}_2\text{O}_5$  (mol%,  $x = 0, 2.5, 5$ , denoted by 20P- $x$ Si) glasses were obtained by melt-quenching. Glass batches were prepared by manually mixing MgO (99.0%), CaCO<sub>3</sub> (99.5%), H<sub>3</sub>PO<sub>4</sub> (85% liquid), SiO<sub>2</sub> (99.0%) and Nb<sub>2</sub>O<sub>5</sub> (99.9%), which were subsequently dried under an infrared lamp overnight and then stored at 140°C. All the reagents were purchased from Kishida Chemical Co., Japan. The batches were melted in a platinum crucible at 1500°C for 30 minutes and the melts were quenched by rapid squashing between two stainless-steel plates. The glass transition ( $T_g$ ) and crystallization temperatures ( $T_c$ , defined as the onset of crystallization) of 20P- $x$ Si were determined by differential thermal analysis (DTA; heating rate: 5 K/min, Thermoplus TG8120, Rigaku). The glasses structures were investigated by solid-state <sup>31</sup>P magic angle spinning nuclear magnetic resonance (MAS-NMR, JNM-ECA600II, JEOL, 242.955 MHz), and laser Raman spectra with range from 220 to 1300 cm<sup>-1</sup> (NRS-3300, 532.08 nm, 6.4 mW, JASCO). <sup>31</sup>P MAS-NMR was measured in a 3.2 mm rotor spinning at 15 kHz with single-pulse experiments using 0.1 μs pulses (256 in total) spaced by 5 s and using ammonium dihydrogen phosphate as a reference (1.0 ppm). The spectra were reconstructed with a Gaussian fit. To examine the crystallization behaviors of the glasses, the resulting 20P- $x$ Si were reheated at 800°C

(heating rate: 5 K/min) for 3 h (denoted by 20P-*x*Si-C). Crystalline phases were analyzed by powder X-ray diffractometry (XRD, X'pert-MPD, PANalytical).

Powders of glasses and crystallized glasses were obtained by grinding and sieving (125 – 250  $\mu\text{m}$ ). A releasing test was examined by immersing 15 mg of the samples in 15 mL of 50 mM Tris buffer solution (TBS) at 37°C and pH 7.4 over 7 days. The concentrations of  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{P}^{5+}$ ,  $\text{Si}^{4+}$  and  $\text{Nb}^{5+}$  ions in TBS were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, ICPS-7510, Shimadzu). The molar releasing fraction of the different elements was calculated using the following equation [8,16]:

$$\text{Release rate (\%)} = \frac{(a/M_{wa}) \times 10^5}{(Frac_a \times M_{w,glass}) / (m_{glass} \times V_{solution})} \quad (1)$$

where  $a$  is the concentration of the element of interest in  $\text{mg} \cdot \text{L}^{-1}$ ;  $M_{wa}$  is the atomic weight of the ion;  $Frac_a$  is the nominal molar fraction of the element in the glass; and  $M_{w,glass}$ ,  $m_{glass}$  and  $V_{solution}$  are the molecular weight, the mass of the sample soaked, and the volume of TBS, respectively. Glass powders after being soaked in TBS for 7 days were observed by scanning electron microscopy (SEM, JSM-6301F, JEOL)

### 3. Results

The glasses exhibited two  $T_g$  values (denoted by  $T_{g-1}$  and  $T_{g-2}$  hereafter), at

approximately 604°C and 662°C, respectively.  $T_c$  value of the glasses were approximately 710°C.  $T_g$ ,  $T_c$  and glassification degree (GD), which was calculated using  $(T_c - T_{g-1}) / T_{g-1}$  (K/K) [17], showed no significant difference between the glasses. GD of the glasses were calculated with  $T_{g-1}$ . The values were approximately 0.12.

$^{31}\text{P}$  MAS-NMR spectra, as presented in Fig. 1, showed a sole peak between 10 and -10 ppm, assigned to  $Q_p^0$  group. The peak top position and full width of half maximum (FWHM) of peak for the glasses were approximately 1.6 ppm and 8 ppm respectively. No significant differences between the glasses were observed.

Laser Raman spectra of the glasses are shown in Fig. 2(A), and FWHM of 840 and 965  $\text{cm}^{-1}$  are shown in Fig. 2(B). The phosphate group in the glasses showed Raman bands corresponding solely to the  $Q_p^0$  group [10]: the symmetric stretching of the O-P-O bending modes of the  $Q_p^0$  at 430  $\text{cm}^{-1}$ , the symmetric stretching of the P-O bonds of the  $Q_p^0$  at 590  $\text{cm}^{-1}$  and the  $(\text{PO}_4)_{\text{sym}}$  stretching mode of the non-bridging oxygen in  $Q_p^0$  at 965  $\text{cm}^{-1}$ . The vibrations at 840  $\text{cm}^{-1}$  corresponded to the symmetric stretching of orthosilicate ( $Q_{\text{Si}}^0$ ) [18,19] and  $\text{NbO}_4$  tetrahedral group [20]. There was almost no significant difference in the FWHM of  $Q_p^0$  (965  $\text{cm}^{-1}$ ) between the glasses. On the other hand, the FWHM of the bands corresponding to  $Q_{\text{Si}}^0$  and  $\text{NbO}_4$  (840  $\text{cm}^{-1}$ ) increased from 68 to 82 ppm with increasing  $\text{SiO}_2$  content in the glasses.

When 20P-*x*Si were reheated at 800°C, they were crystallized (20P-*x*Si-C), as shown in Fig. 3. The 20P-0Si-C showed XRD peaks corresponding to  $\beta$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> (ICDD card: 70-2065), Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> (ICDD card: 75-1491) and Mg<sub>3</sub>Ca<sub>3</sub>(PO<sub>4</sub>)<sub>4</sub> (ICDD card: 73-1182). With increasing SiO<sub>2</sub> content in the glasses, Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> peaks disappeared and the intensities of  $\beta$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> peaks decreased. Niobate and/or silicate crystalline phases were not observed.

Figure 4 shows the ions-released percentages from 20P-*x*Si or 20P-*x*Si-C into TBS, relative to the original amount in the glasses or crystallized glasses. The ions-release percentage of phosphorus ion from 20P-*x*Si at day 7 decreased significantly from 22% to 14% corresponding to the SiO<sub>2</sub> content in the glasses. SEM observation of the surface of 20P-*x*Si after 7 days of soaking suggested that a gel-like layer formed on the surface of the glasses. The percentages of phosphorus ion released from 20P-2.5/5Si-C were larger than that released from 20P-0Si-C; those of magnesium and calcium ions were at almost same levels, whereas silicate and niobate ions were detected to be almost 0%.

#### 4. Discussion

The glassification degree (GD) of 20P-*x*Si was around 0.12. The value is larger

than that of TiCa-PIGs (0.08) [3] and NbCa-PIGs (0.09) [2]; this indicates better glass forming ability. 20P-*x*Si showed several glass transition temperatures, which indicate the coexistence of several glass-network formers, such as phosphate, silicate, niobate/niobia [20,21] and magnesia [9,10]. Phosphate and silicate are well-known glass-network formers. Raman spectra showed that niobate/niobia in the glasses takes the form of tetrahedral NbO<sub>4</sub> (Fig. 2(A)), which acts as a network former [20] to form P-O-Nb bonds [22,23]. Brow reported that invert glasses do not have a continuous random network and their structures consist of short phosphate groups (*i.e.*  $Q_p^0$  and  $Q_p^1$ ) and modifier ions linked through the non-bridging oxygen [24]. 20P-*x*Si consists of  $Q_p^0$  (PO<sub>4</sub>),  $Q_{Si}^0$  (SiO<sub>4</sub>) and NbO<sub>4</sub> tetrahedra and modifier ions, such as Mg<sup>2+</sup> and Ca<sup>2+</sup> ions. According to Dietzel's rule, MgO is an intermediate oxide [25]. MgO acts as a network former in phosphate glasses with high MgO content, consisting of  $Q_p^0$  and  $Q_p^1$  groups [9,10]. Therefore, MgO in 20P-*x*Si acts as a network former to form P-O-Mg bonds [8,16]. The cumulative network forming ability of phosphate, silicate, niobate/niobia and magnesia at low content of phosphate (*i.e.* 20 mol%) might explain the presence of only orthophosphate group ( $Q_p^0$ ) and larger glassification degree than that of Ti/NbCa-PIGs.

There were no significant differences in the peak top positions and FWHMs of

$Q_p^0$  in  $^{31}\text{P}$  MAS-NMR spectra (Fig. 1), irrespective of the  $\text{SiO}_2$  content. This implies that the coordination status of the  $Q_p^0$  group does not change with incorporation of  $\text{SiO}_2$ ; silicate makes no bond or coordination with phosphate group. The Raman band between  $840$  and  $880\text{ cm}^{-1}$  can be considered the symmetric stretching of orthosilicate ( $Q_{\text{Si}}^0$ ) [18,19] in common silicate glasses. In case of present orthophosphate invert glasses, Raman band of  $\text{NbO}_4$  also observed in  $840\text{ cm}^{-1}$  [20]. The FWHM  $840\text{ cm}^{-1}$  (Fig. 2(B)) increased significantly with increasing  $\text{SiO}_2$  content, indicating the diversification of coordination status in  $Q_{\text{Si}}^0$  and  $\text{NbO}_4$ . This may imply  $Q_{\text{Si}}^0$  and  $\text{NbO}_4$  coordinate with each other and form Si-O-Nb bonds [26]. Originating from this glass structure, 20P- $x$ Si-C is considered to consist of  $Q_p^0$ -based crystals with the residual glassy phases containing silicate and niobate.

Ions-releasing percentage of 20P- $x$ Si at day 7 was approximately 13%. This value is comparably larger than that of Ti/NbCa-PIGs (around 4–7% at day 7 [3]). This indicates the chemical durability of 20P- $x$ Si is slightly lower than that of Ti/NbCa-PIGs. Ti/NbCa-PIGs contain large amounts of P-O-Ti/Nb bonds [2,3], which were reported to improve the chemical durability of phosphate glasses [23,27].  $\text{Mg}^{2+}$  ion in phosphate invert glasses containing intermediate oxides (*i.e.*  $\text{TiO}_2$  or  $\text{Nb}_2\text{O}_5$ ) preferentially coordinates with  $Q_p^0$  group to form P-O-Mg bonds [16], and degrades the chemical

durability of the glasses [16,28,29], since P-O-Mg bonds are similar to Si-O-Mg bonds and weaken the glass network structure [30] and the resistance to hydrolysis [31]. As the only phosphate group in 20P- $x$ Si is  $Q_p^0$ , P-O-Mg bonds are preferentially formed in the structure. Therefore, the chemical durability of 20P- $x$ Si was comparably lower than that of Ti/NbCa-PIGs [2,3]. Gel-like layers on the glass surfaces were observed after soaking TBS. With increasing SiO<sub>2</sub> content, the chemical durability of 20P- $x$ Si was slightly improved, since the field strength of Si (1.57 valence / Å<sup>2</sup>) is larger than that of Ca (0.33 valence / Å<sup>2</sup>) or Mg (0.53 or 0.45 valence / Å<sup>2</sup>, 4-fold or 6-fold coordination, respectively) [25]. The amounts of magnesium and calcium ions released from 20P- $x$ Si-C were smaller, compared with 20P- $x$ Si, due to the small amounts of soluble crystals. However, the releasing amount of phosphorus ions increased after the heat-treatment. The residual glassy phase may induce phase separation; the phases might be phosphate and niobium-silicate network. Phosphate network contains P-O-Mg bonds, which are weak from the view point of the chemical durability of the glasses [16,28,29], whereas silicate network contains Nb-O-Si bonds which improve the chemical durability [26].

## 5. Concluding remarks

Orthophosphate MgO-CaO-P<sub>2</sub>O<sub>5</sub>-SiO<sub>2</sub>-Nb<sub>2</sub>O<sub>5</sub> invert glasses and crystallized glasses were successfully prepared, and their structures and releasing behaviors were examined. The glasses showed several  $T_g$  values, indicating the coexistence of several glass-network structures, such as  $Q_p^0$ ,  $Q_{Si}^0$  and NbO<sub>4</sub> tetrahedral groups. MgO in the glasses was also considered to act as a network former to cross-link short glass-network forming groups (*i.e.*  $Q_p^0$ ,  $Q_{Si}^0$  and NbO<sub>4</sub>). In particular, silicate and niobate/niobia coordinate with each other to form Si-O-Nb bonds. The crystallized glasses included orthophosphate crystal phases, such as  $\beta$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and Mg<sub>3</sub>Ca<sub>3</sub>(PO<sub>4</sub>)<sub>4</sub>, without silicate and niobate crystals. The chemical durability of 20P- $x$ Si was lower than that of Ti/NbCa-PIGs, since magnesium in phosphate invert glasses formed P-O-Mg bonds, which favor hydrolysis. The chemical durability of 20P- $x$ Si was slightly improved by addition of SiO<sub>2</sub>, since the field strength of Si is larger than that of Ca or Mg. 20P- $x$ Si is expected to enhance bone formation by ions released from the glasses, such as magnesium, silicate and niobium ions. These results are expected to be useful for designing novel biomedical materials.

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## Figure captions

Figure 1:  $^{31}\text{P}$  MAS-NMR spectra of 20P- $x$ Si.

Figure 2: (A) Raman spectra of 20P- $x$ Si and (B) FWHM of 840 and 965  $\text{cm}^{-1}$  for 20P- $x$ Si, as a function of  $\text{SiO}_2$  content in the glasses.

Figure 3: XRD patterns of 20P- $x$ Si-C.

Figure 4: Percentages of ions in the TBS after soaking 20P- $x$ Si or 20P- $x$ Si-C, relative to the total amounts for  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{P}^{5+}$ ,  $\text{Si}^{4+}$  and  $\text{Nb}^{5+}$  ions as a function of  $\text{SiO}_2$  content in the glasses or crystallized glasses. The error bar represents the standard deviation. Inset shows the SEM images of 20P- $x$ Si surface after being soaked in TBS for 7 days.

## Figures

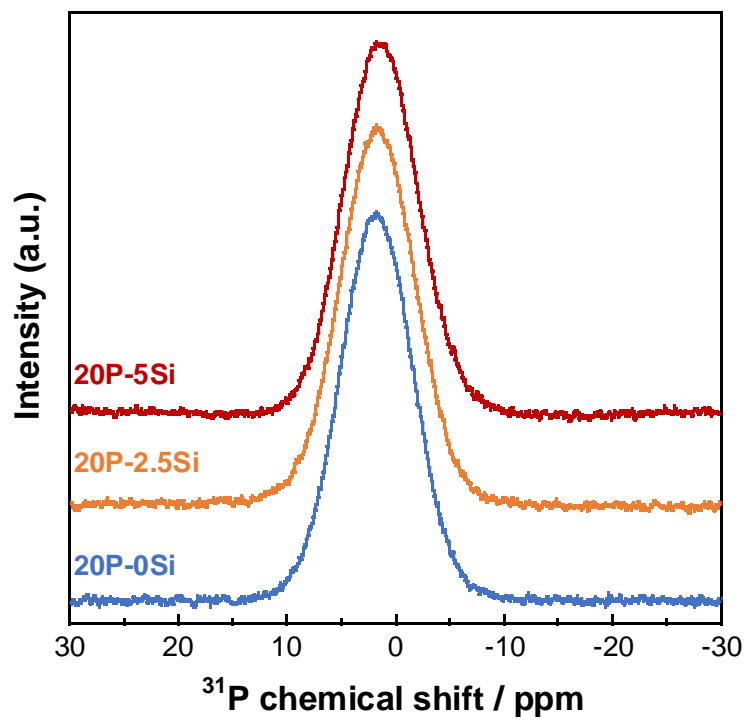


Fig. 1

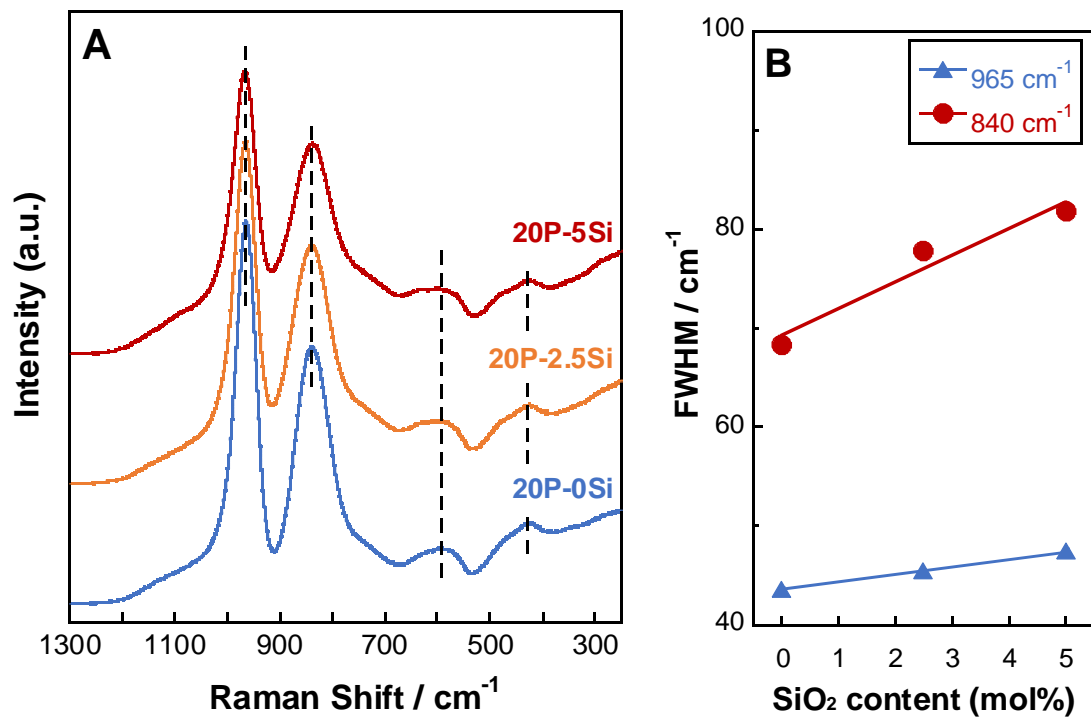


Fig. 2

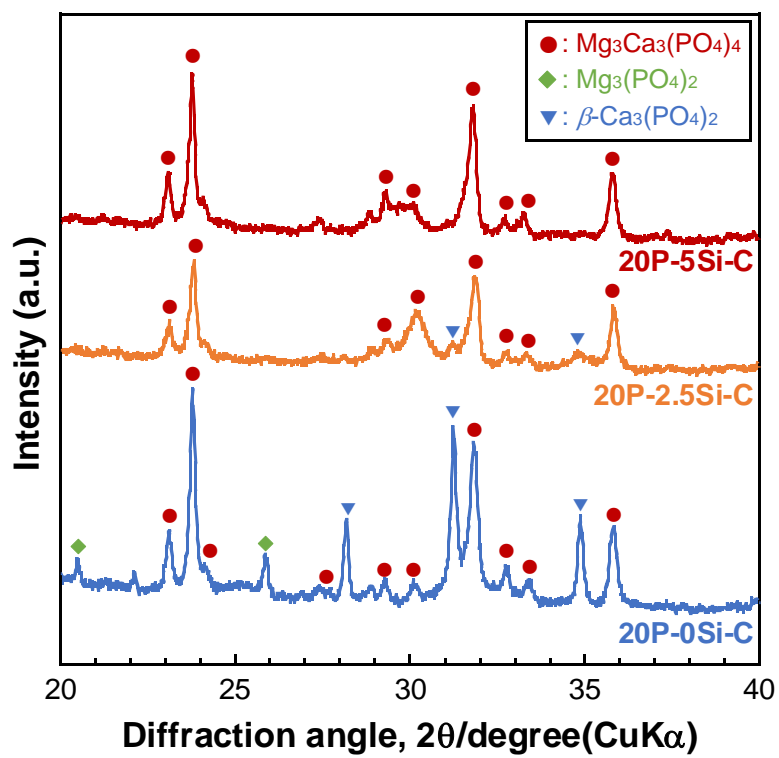


Fig. 3

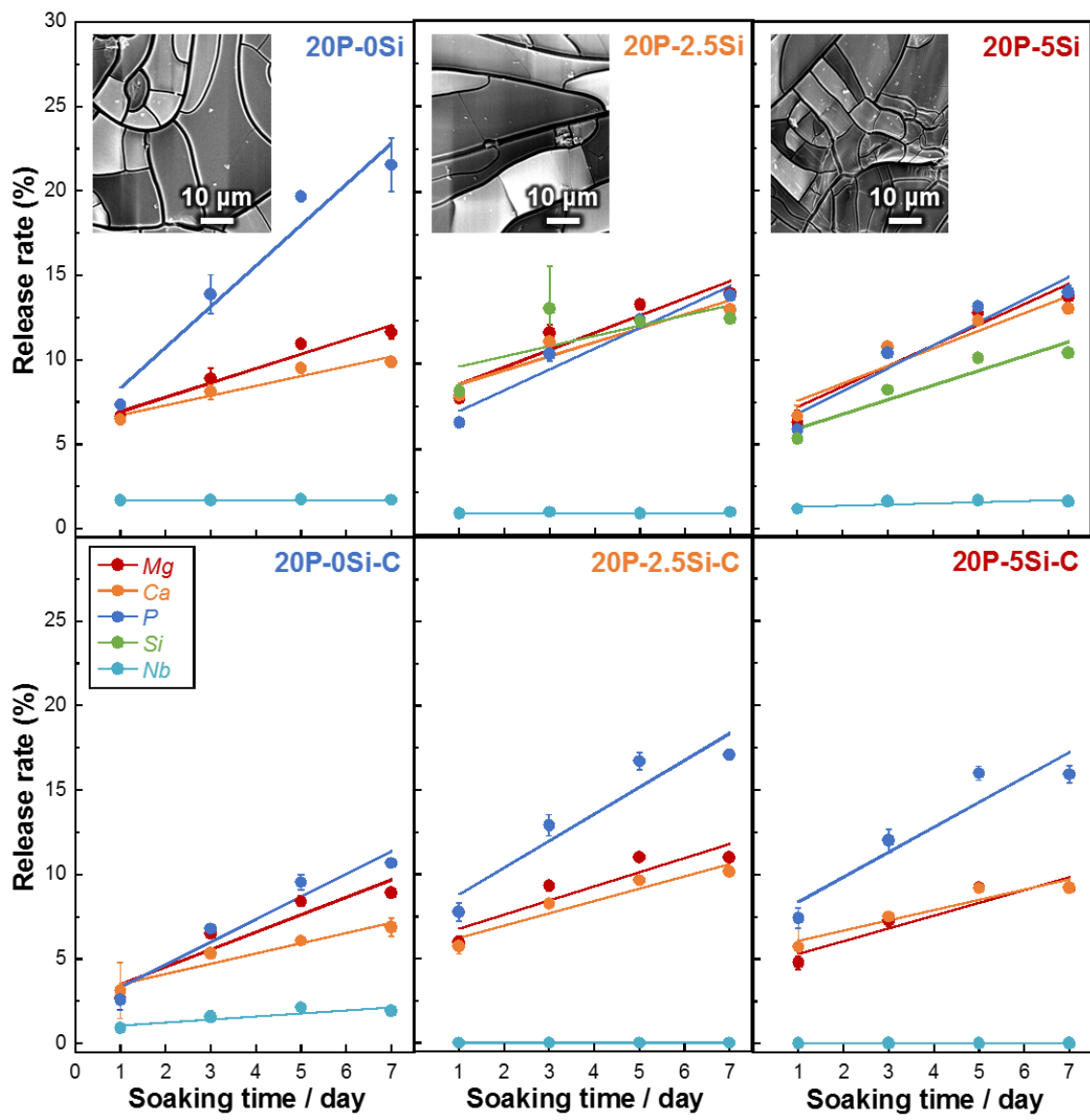


Fig. 4