

Effect of Strontium Additions on Crystalline Phases and Chemical Solubility of Fluorapatite Glass-Ceramics

Isabelle Denry, Julie A. Holloway.

University of Iowa College of Dentistry, Department of Prosthodontics and Dows Institute for Dental Research.

Statement of Purpose: Strontium has recently generated considerable interest, due to its reported efficacy for preventing bone resorption in the treatment of osteoporosis. Strontium is primarily incorporated by ion-exchange onto the apatite crystal surface in newly formed bone. However, when administered orally, even at high doses (3 mmol Sr per day for 13 weeks), less than one calcium ion can be substituted by strontium in the apatite structure. As a result, several research groups have focused on the development of Sr-substituted apatite-based ceramics for biomedical applications, either as bulk ceramics, glass-ceramics, scaffolds or cements, all of which are in direct contact with the surrounding tissues, thereby ensuring a better release. The progressive substitution of strontium for calcium in the apatite structure is associated with a linear increase in the lattice constants, due to the slightly larger ionic radius of strontium. The substitution is also associated with the creation of lattice defects, vacancies and distortions which affect the surface properties in terms of hydration layers and surface charges. It was also reported that the solubility of Sr-substituted apatite in Hank's balanced synthetic fluid at 37°C and its calcium and strontium release capabilities are significantly higher than that of hydroxyapatite. Our goal was to investigate the effect of strontium additions on the phase composition and chemical solubility of fluorapatite glasses.

Methods: Four fluorapatite glass compositions in the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-MgO-Na}_2\text{O-K}_2\text{O-CaO-CaF}_2$ system, with increasing amounts of strontium oxide (A:0, B:12, C:18 and D:24 mol.%) in partial replacement for calcium oxide, were prepared by twice melting at 1525°C for 3h. After the second melt, glasses were cast into cylindrical ingots. Differential thermal analyses were performed on powdered glasses to determine glass transition and crystallization temperature. Disc-shaped specimens (1.2 mm thick, 10 mm in diameter) were sectioned from the ingots. Specimens were heat treated at various temperatures ranging from 775 to 900°C for 1h, and analyzed by x-ray powder diffraction (Rigaku SmartLab). The density of the glass-ceramics was measured by Archimedes' method. The chemical solubility was determined on powders after incubation for 120h at 37°C in either TRIS-HCl buffer at pH 7.4 or citric acid buffer at pH 3.0, to create either moderate or extreme aging conditions, according to ISO standard 10993-14. The pH of the buffer solutions was measured before and after incubation. Specimens were dried at 80°C until no further weight loss was observed, the percent weight loss was then calculated for each composition and each buffer. A variable pressure SEM (VP-SEM, Hitachi 3400) coupled with a back-scattered electron detector, was used to perform semi-quantitative EDS analyses of the powders before and after incubation (Bruker AXS microanalyzer).

Results: XRD analyses revealed the formation of both strontium-substituted fluorapatite and strontium-substituted akermanite in the strontium-containing glasses. Differential thermal analyses of powdered

glasses showed that the crystallization temperature of Sr-substituted fluorapatite varied only slightly amongst compositions. Meanwhile the crystallization temperature for Sr-substituted akermanite increased linearly with strontium content. The density of the glass-ceramics after heat treatment at 775°C/1h increased linearly ($R^2=0.985$) with Sr content from 2.951 ± 0.005 for composition A to 3.353 ± 0.021 for composition D. The pH after incubation in TRIS-HCl buffer increased slightly for all compositions. The pH after incubation in citric acid buffer (pH 3) increased markedly for composition D (7.11 ± 0.42) and was highest for composition A (8.58 ± 0.42). The chemical solubility increased as the amount of strontium in the composition increased, reaching a maximum of 2.6 ± 1.2 wt.% in TRIS-HCl buffer and 10.4 ± 0.6 wt.% in citric acid buffer, both for composition D (Figure 1). The weight loss in citric acid buffer for composition A (4.2 ± 1.2) was not significantly different from that of a synthetic fluorapatite control (4.6 ± 0.6 ; Clarkson Chromatography, Inc.).

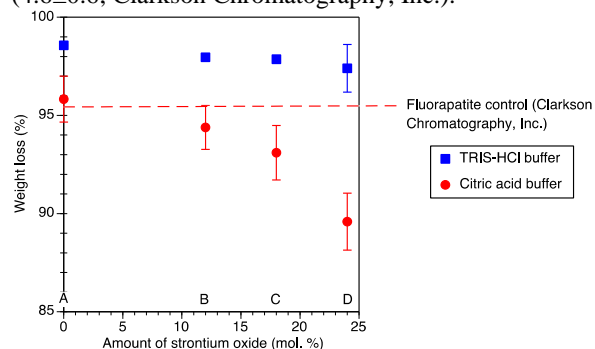


Figure 1. Chemical solubility as a function of strontium content in TRIS-HCl and citric acid buffer (120h at 37°C, according to ISO 10993-14). EDS analyses after incubation in citric acid buffer revealed that the Sr-free composition (A) underwent losses in fluorine, sodium and magnesium. Composition B exhibited losses (0.2 to 1.4 at.%) in fluorine, sodium, calcium, strontium, magnesium and potassium. Composition C showed losses (0.3 to 1.8 at.%) in all above species except fluorine. Moderate losses in fluorine and sodium (0.1 to 0.2 at.%) were recorded for Composition D. All compositions, with the exception of A, exhibited very large variations in the amount of silicon after incubation.

Conclusions: Strontium additions in this system led to crystallization of Sr-substituted fluorapatite and Sr-akermanite ($(\text{Ca,Sr})_2\text{MgSi}_2\text{O}_7$). The chemical solubility increased with the amount of strontium in the composition in both TRIS-HCl buffer and citric acid buffer. Various species were released during incubation including strontium and calcium. The large variations in silicon content for B, C and D could indicate that the glass network was at various stages of dissolution. Supported by NIH-NIDCR R01 DE19972.