Topotaxial replacement of chlorapatite by hydroxyapatite during hydrothermal ion exchange

K. Yanagisawa,1, * J.C. Rendon-Angeles,1 N. Ishizawa,2 and S. Oishi3

1Research Laboratory of Hydrothermal Chemistry, Kochi University, Kochi 780-8520, Japan
2Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan
3Department of Environmental Science and Technology, Faculty of Engineering, Shinshu University, Nagano 380-8553, Japan

ABSTRACT
Exchange of Cl− by OH− in synthesized chlorapatite single crystals was investigated under hydrothermal conditions. Hydrothermal treatments were performed at various temperatures from 200 to 500 °C, for intervals between 3 and 96 h in KOH or NaOH solutions. Ion exchange of Cl− in the chlorapatite crystals was completed at low temperature (500 °C) for a short time (12 h) in 6.25 M KOH solution, and resulted in the formation of hydroxyapatite. The rate of ion exchange was accelerated by increasing the reaction temperature and/or concentration of the alkaline solutions. That the converted crystals were single crystals of hydroxyapatite was confirmed by X-ray precession photographs. The hydroxyapatite single crystals that formed from the chlorapatite single crystals by the topotaxial ion exchange under alkaline hydrothermal conditions had a characteristic texture, exhibiting channels on the surfaces and tunnels inside, both along the c axis of the crystals. A dissolution and precipitation process is proposed for the ion-exchange reaction conducted under hydrothermal conditions.

INTRODUCTION
Calcium apatites occur in nature both biologically and as minerals. Apatites have found important uses in several industrial applications, such as fertilizer in the agricultural industry and phosphor in the lighting industry. Calcium hydroxyapatite [Ca10(PO4)6(OH)2, hereafter referred to as HAP] is the most important member of the phosphate mineral group, mainly because it is the prototype of the inorganic material in hard tissues such as bone and teeth, and is also regarded as an important implant material with significant clinical potential (e.g., Sänger and Kuhs 1992; Hench 1991). Thus, much research concerned with HAP has been carried out in fields such as crystallography, mineralogy, medical science, and material science.

In recent years, some work has been conducted to evaluate the possibility of employing HAP as a precursor material for the removal of heavy metal ions from waste water (Reichert and Binner 1996; Suzuki et al. 1981). This possibility is based on the apatite structure, which has the ability to undergo a series of isomorphous substitutions involving both cations and anions (Narasaraju and Phebe 1996). According to a review by these authors, Sr2+, Ba2+, Pb2+, Zn2+, and Cd2+ substitute for Ca2+ in HAP, and F−, Cl−, and I− may substitute for OH−. Furthermore, CO32− may substitute not only for OH− but also for PO43− groups (Legeros et al. 1968; Driessens et al. 1983). Studies on the ionic substitutions in HAP are important in medical science, because biological apatite includes various foreign ions.

Because the natural apatite minerals and biological apatite include OH−, F−, and Cl− in their structure, the solid solutions in the ternary system of HAP, chlorapatite [Ca10(PO4)6Cl2, hereafter referred to as CIAP], and fluorapatite [Ca10(PO4)6F2, hereafter referred to as FAP] have been well studied, both crystallographically (e.g., Sudarsanan et al. 1972; Sudarsanan and Young 1978; Tse et al. 1973; Hughes et al. 1990) and experimentally (e.g., Elliott and Young 1967; Rai et al. 1979, Maiti and Freund 1981; Latil and Maury 1977; Simpson 1968; Stearns and Berndt 1973; Higuchi et al. 1974). As for the HAP-CIAP system, Rai et al. (1979) showed the existence of a homogeneous solid solution series over the entire compositional range. According to the papers mentioned above, these solid solutions were prepared by reactions that did not include an ion exchange.

Elliott and Young (1967) provided the first evidence of the solid-state ion exchange in the apatite structure. They converted CIAP single crystals to HAP single crystals by heating at 1300 °C for 2 weeks in water vapor at atmospheric pressure. Neutron activation analysis and X-ray diffraction (XRD) precession photographs demonstrated that the reaction products were essentially single crystals of HAP, although a small amount of Cl remained in the crystals.

The ion-exchange rate of Cl− in CIAP by OH− must depend on the concentration of OH− in the ion-exchange medium. It is well known that the ion product of water increases with the increase in temperature and pressure (density). Thus, the concentration of OH− must increase under hydrothermal conditions at high temperature and pressure. In fact, Brenan (1994) showed that diffusion coefficients of anions in the apatite structure measured under hydrothermal conditions at 1 GPa were higher.

*E-mail: yanagi@cc.kochi-u.ac.jp