

## 0832 Hydroxyapatite, fluorapatite, chlorapatite and calcium fluoride solubility by solid titration

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The solubility isotherm (S) of hydroxyapatite (HAp) and fluorapatite (FAP) are of fundamental importance in saliva chemistry, dental caries and related contexts. It has previously been shown that S[HAp] is substantially lower than is commonly reported, and of different slope, probably due to the effects of incongruent dissolution. The role of other species in these systems requires elucidation. **Objectives:** Ascertain the solubility isotherms of HAp in the presence of fluoride, of FAp itself, and of  $\text{CaF}_2$ . **Methods:** The solid titration technique of Leung & Darvell (J Chem Soc Faraday Trans, 1991) was used at 37°C in 100 mM KCl for HAp, FAp and  $\text{CaF}_2$ , and for HAp with 1 mM KF added. Fluoride-containing runs were repeated in wax-lined vessels. X-ray diffraction was used to identify precipitates. **Results:** The S[HAp] reported by Chen *et al.* (Arch Oral Biol, 2004) was reconfirmed. However, the solid appearing at pH < 3.9 is not brushite ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ), but may be a calcium-deficient chlorapatite (ClAp). Adsorption or reaction with the glass of the reaction vessel gave anomalous results in the presence of fluoride; wax-coating resolved the problem. S[ $\text{CaF}_2$ ] was as theoretically-expected; S[FAP] was correct relative to that for HAp, only slightly less soluble. Adding 1 mM KF affected the apparent S[HAp] in similar fashion at pH > 3.7, presumably by forming FAp, but  $\text{CaF}_2$  remains possible. **Conclusions:** The solid titration method is confirmed reproducible and to yield HAp for pH 3.9 ~ 5.2. Its applicability to other solids is demonstrated. Below pH 3.9, 100 mM KCl appears to be enough to make ClAP the stable phase, while the otherwise expected brushite did not appear. Glass apparatus appears to be problematic when fluoride is present, which may have broad implications for such work. We are grateful to the Paffenbarger Research Centre for the supply of the FAp.

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