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# The effect of selenium on fluoride – clay interactions: possible environmental health implications

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## Abstract

Previous epidemiological studies have shown that dental fluorosis is endemic in the lowland, dry zone of Sri Lanka, which is considered to be an area in which excessive quantities of fluorides are present in the drinking water supplies. It has been found that kaolinitic clay forms a suitable raw material in the defluoridation of water.

It is shown that there is a noticeable effect of selenium and media pH on the reactions involved in the interaction of fluoride with clay. In this study, 1 mM fluoride solutions containing $SeO_3^{2-}$ (selenite) concentrations of 0 mM, 0.1 mM, 0.5 mM and 1 mM were used in the reactions with kaolinitic clay. The effect of pH was monitored in the range 4 to 8. It was observed that fluoride adsorption was maximum at a pH of 5.6 without either $SeO_3^{2-}$ or $SeO_4^{2-}$, the adsorption capacity being 15.2 μmol $F^-$ $g^{-1}$ clay. However, when the $SeO_3^{2-}$ concentration was increased up to 0.5 mM at this optimum pH, the adsorption capacity reduced to 12.8 μmol $F^-$ $g^{-1}$ clay. Monitoring of the effect of $SeO_4^{2-}$ and media pH on fluoride adsorption showed that when the $SeO_4^{2-}$ concentration increases from zero to 0.1 mM, there is a reduction of fluoride adsorption capacity. However, when the $SeO_4^{2-}$ concentration is further increased from 0.1 mM to 1.0 mM, there was an increase in the fluoride adsorption capacity, indicating a more consistent effect of $SeO_3^{2-}$ on fluoride-kaolinitic clay interaction than $SeO_4^{2-}$.

Fluoride concentrations in drinking water supplies have a marked effect on dental health and the geochemistry of selenium appears to play an important role in the geochemical mobility of fluoride ions.

## Introduction

Many water supply schemes, particularly in developing countries where dug wells and tube wells form the major water source, contain excess fluorides normally detrimental to dental health. Crounse *et al.*, (1983) showed that the effect of molybdenum may suppress dental decay while Se at higher levels may promote dental decay. Selenium is also known as an element influencing protection against cancer (Schrauzer, 1979; Baumgartner, 1979; Janson, 1980; Weerasooriya *et al.*, 1987). It has been previously shown that kaolinitic clay could be used as a starting material for the defluoridation of fluoride-rich drinking waters at village level (Jinadasa *et al.*, 1988).

As an essential element in animal nutrition, Se is required in small amounts and this varies within very narrow limits producing toxicity symptoms at higher concentrations. Seleniferous soils enrich vegetation in selenium which subsequently may become toxic to grazing animals. During the chemical weathering of rocks, Se oxidation as well as its solubility, are controlled by the oxidation – reduction regime and by the pH of the environment. Selenium ions resulting from oxidation processes are able to migrate unless they are absorbed on mineral or organic particles (Cooper *et al.*, 1974; Johnson, 1975). As a result, Se particularly when present in the $SeO_4^{2-}$ form can enter into the ground water table. It can also exist in soils as biselenite ($HSeO_3^-$), selenate ($SeO_4^{2-}$), selenite ($SeO_3^{2-}$), elemental selenium ($Se^0$), sparingly soluble metal selenides ($Se^{2-}$) and complex forms in soil organic matter. Under acid, well drained soil conditions, $HSeO_3^-$ is more abundant than $SeO_4^{2-}$ and is strongly adsorbed on iron oxides or forms stable complexes with FeOOH (Johnson, 1975). Ylaranta (1983), reported that selenite was sorbed strongly by a clay soil. Frost and Griffin (1977), found that the decrease in selenite sorption with increasing pH was much more gradual for kaolinite than for montmorillonite.

Stoichiometric release of $OH^-$ from kaolinite by $F^-$ has been reported by Vickman and Bray (1941), who concluded that $F^-$ replaces the $OH^-$ ions found on the clay. Other studies have shown that with the degradation of the mineral structure, Al is released into the solution from phyllosilicate clays and amorphous aluminium hydroxy oxides, with the concomitant entry of fluoride into the mineral structure (Perrott *et al.*, 1967; Sampson, 1952;

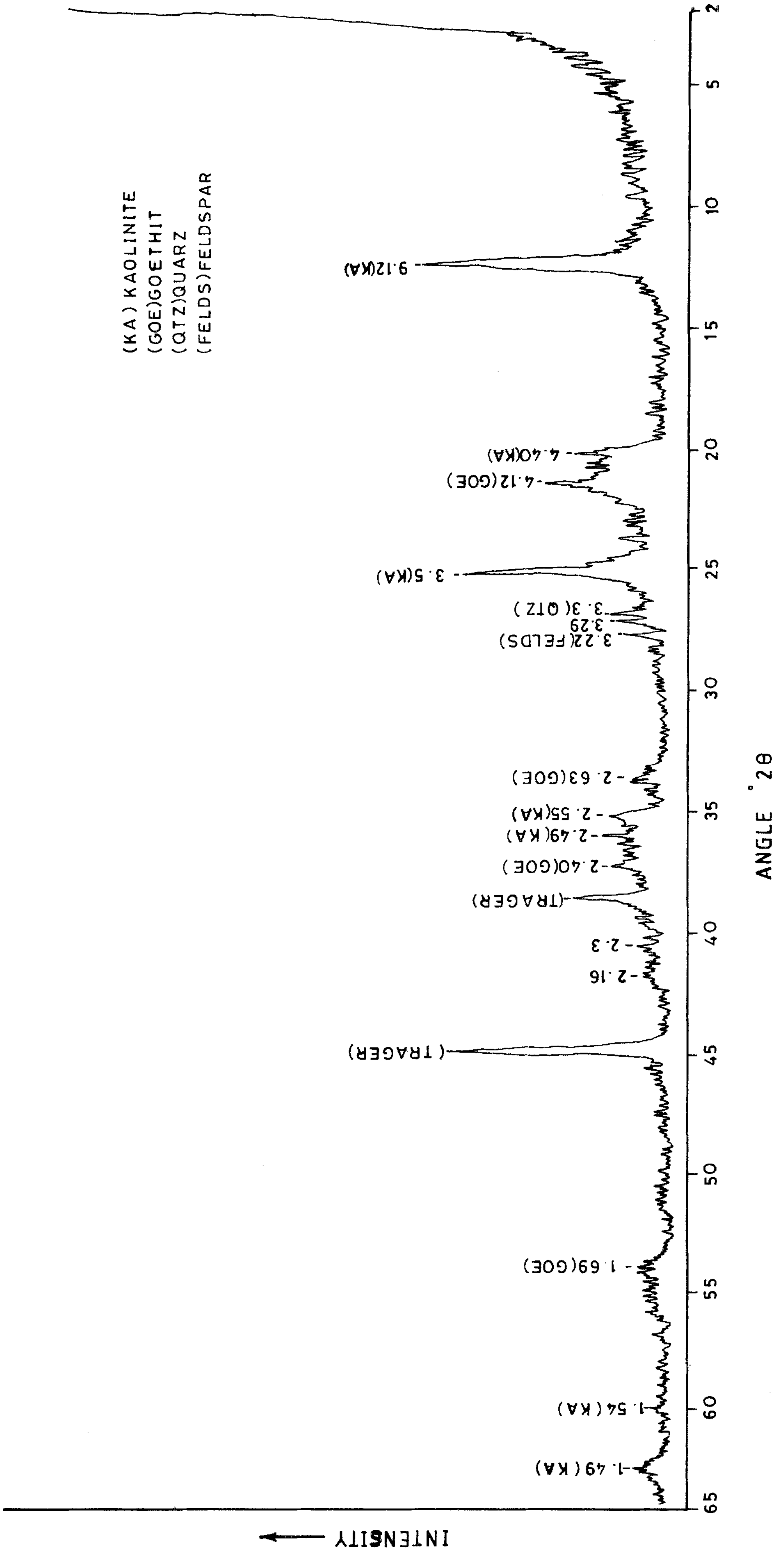

**Figure 1** *X-ray diffraction pattern for clay.*

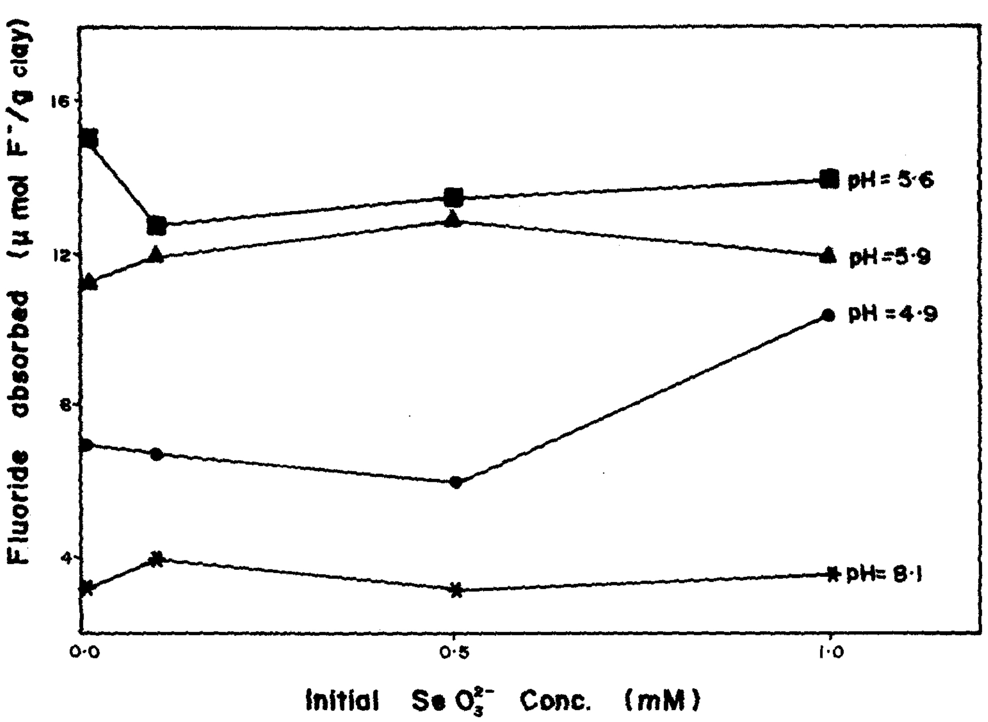

**Figure 2** *Fluoride adsorption with* $SeO_3^{2-}$ *and media pH.*

Semmens and Meggy, 1966). The formation of cryolite ($Na_3AlF_6$) after treatment of clay minerals with $F^-$ also supported the idea that $F^-$ did not simply replace $OH^-$ in the lattice but actually decomposed it (Omuetti and Jones, 1977).

Since both selenium and fluoride are of importance in environmental geochemistry and health, it is intended that these studies would provide further information on the pathways of the two elements. Selenium is known as an element adversely affecting the health of humans and animals when either deficient or present in excess while fluoride affects dental health, when found in very low or very high concentrations.

## Materials and Methods

### *Sample collection and preparation*

The clay samples used for the present study were collected from the kaolinitic region at Pussellawa in the Highlands of Sri Lanka. The samples were air dried and the powdered material passing through the +230 mesh sieve was used for the study. A separate clay sample was selected for mineral analysis.

### *Mineral analysis of clay*

Preliminary investigations of the X-ray diffraction pattern (using the Shimadzu model XRD meter) for the Pussellawa clay were carried out (Figure 1).

### *Investigations on* $SeO_3^{2-}/SeO_4^{2-}$ *and media pH*

The adsorption of the $F^-$ on to clay was investigated in the presence of $SeO_3^{2-}$ or $SeO_4^{2-}$. In this experiment 1 mM fluoride solution containing various concentrations of either $SeO_3^{2-}$ or $SeO_4^{2-}$ (0 mM, 0.1 mM, 0.5 mM and 1mM) were used. The ratio of clay to solution was 1:20. In order to keep the pH between 3.8 and 8.2, buffered NaOAc/HOAc and $Na_2HPO_4/NaH_2PO_4$ were used. The fluoride-clay system was equilibrated for 24 hours and the fluoride concentration of the supernatant solution was measured in duplicate samples.

### *Determination of fluoride*

Measurements of fluoride ions were carried out by the use of fluoride specific ion electrode (Orion model 94/09/00) Single junction reference electrode (Orion model 90/01/00) and Orion Ionanalyzer (model 407A).

## Results and Discussion

### *Effect of* $SeO_3^{2-}$ *and* $SeO_4^{2-}$ *and media pH and* $F^-$ *adsorption*

Experiments were conducted to study the variations of fluoride adsorption on to clay in the presence of a range of concentrations of $SeO_3^{2-}$ and $SeO_4^{2-}$ (0 to 1 mM) at pH levels of 4 to 8. As shown in Figure 1 the clay studied consists mainly of kaolinite and goethite. In effect therefore the role of $SeO_3^{2-}$ and $SeO_4^{2-}$ respectively in the fluoride adsorption on clay is investigated.

Figure 2 illustrates the fluoride and selenite interaction on clay at various pH levels. Accordingly, the fluoride adsorption maximum on clay at a pH of 5.6 and at zero $SeO_3^{2-}$ concentration was 15.2 μmol $F^-$ $g^{-1}$ clay. At this optimum pH, when the $SeO_3^{2-}$ concentration was increased, the fluoride adsorption capacity was reduced to a value of 12.8 μmol $F^-$ $g^{-1}$ clay.

Anions such as selenite and phosphate are generally thought to be adsorbed by ligand exchange (Hingston *et al.*, 1968; Parfitt, 1978; Rajan, 1979; Goldberg and Sposito, 1986). This process may involve the two step mechanism

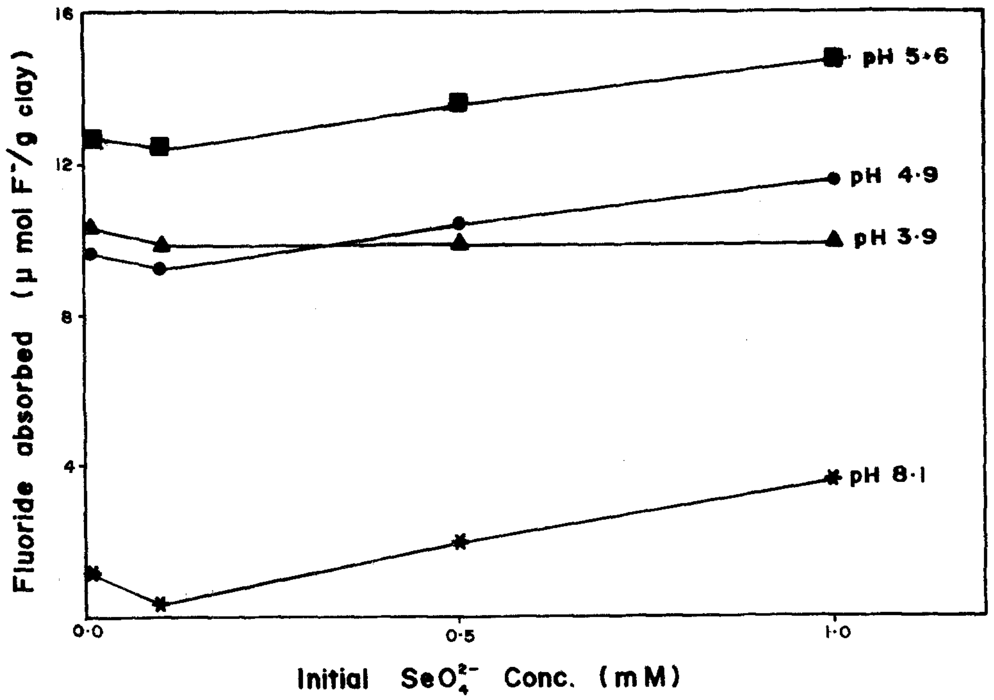

**Figure 3** *Fluoride adsorption with* $SeO_4{}^{2-}$ *and media pH.*

(Yates and Healy, 1975; Cornell and Schindler, 1980).

$$S\text{-}OH + H^+ + SeO_3^{2-} \overset{K_1}{\rightleftharpoons} S\text{-}SeO_3^- + H_2O$$

$$S\text{-}OH + 2H^+ + SeO_3^{2-} \overset{K_2}{\rightleftharpoons} S\text{-}HSeO_3 + H_2O$$

Where S-OH is a surface hydroxyl group and S-$SeO_3$ and S-$HSeO_3$ are the adsorbed selenite species. $K_1$ and $K_2$ are the equilibrium constants. The above reaction suggests that the removal of anions from solution by sorption of clay surface is influenced by the pH of the system, the concentration of available binding sites and the equilibrium anion concentration.

As shown by X-ray diffraction (Figure 1) the clay consists of kaolinite and goethite. Hingston *et al.* (1968) and Hingston (1970) investigated $SeO_3{}^{2-}$ adsorption on goethite and gibbsite and reported on increases in both the pH of the suspension and the negative surface charge on the oxide resulting from adsorption of selenite. Recent studies by Runnels *et al.* (1987) and Martin and Samart (1987) have shown the $SeO_3{}^{2-}$ is adsorbed onto goethite by replacing two S-type (surface) hydroxyl groups (singly coordinated to ferric ions) on the (001) and (010) goethite faces to form bridge complexes of the form FeO(SeO.OH) O.Fe. Frost and Griffin (1977) observed that selenite sorption on the clay minerals kaolinite and montmorillonite was highest at pH 3, decreased at pH 6, and was low at pH 9. These observations are particularly relevant in view of the fact that the samples studied by us contained kaolinite in addition to goethite.

Thus the relative abundance of binding sites in goethite and kaolinite for fluoride adsorption may be reduced in the presence of $SeO_3{}^{2-}$. This fact is illustrated in Figure 2. Barrow (1984) too noted that the lowest fluoride adsorption was at pH 8. He attributed this to the competitive effects of the OH ion.

In a separate study, Hansman and Anderson (1985) have derived the free energy involved in the adsorption of selenite into components from

$$\underset{\text{Net}}{\Delta G} = \underset{\text{intrinsic}}{\Delta G} + \underset{\text{electrostatic}}{\Delta G}$$

and have used electrophoretic mobility of selenite to estimate ΔG electrostatic as a function of pH. These authors obtained a ΔG intrinsic value for selenite as –39.31 KJ $mol^{-1}$. They further stated that this value is favourable for adsorption at low pH and unfavourable at high pH.

Figure 3 illustrates the effect of $SeO_4{}^{2-}$ on fluoride adsorption. It is observed that at all pH levels, and up to a $SeO_4{}^{2-}$ concentration of 0.1 mM, there is a similar pattern for fluoride adsorption capacity, characterized by a decrease. From 0.1 mM up to 1.0 mM $SeO_4{}^{2-}$ however, there appears to be an increase in the fluoride adsorption capacity.

As shown in Figures 2 and 3, it is at pH level of 4.9 that the difference in fluoride adsorption capacity on clay in the presence of $SeO_3{}^{2-}$ or $SeO_4{}^{2-}$ is most marked. Balistrieri and Chao (1987) showed that the effect $SeO_3{}^{2-}$ on goethite is greater than that of $SeO_4{}^{2-}$. Bar Yosef and Meek (1987) observed that the sorption of $SeO_3{}^{2-}$ on kaolinite was greater than that of $SeO_4{}^{2-}$. In view of the fact that the clay material studied consists of kaolinite and goethite (Figure 1) and since the effect of $SeO_3{}^{2-}$ is greater than that of $SeO_4{}^{2-}$, the former is the more important species affecting fluoride-clay interaction.

## Conclusions

The maximum pH for fluoride adsorption on the kaolinite-goethite clay was observed at pH 5.6. At this pH, the fluoride adsorption capacity was reduced in the presence of selenite, or selenate up to a concentration of 0.1 mM. These species can bind with the clay surface thereby reducing the binding sites available for fluoride adsorption. The variation of the fluoride adsorption capacity at the $SeO_3{}^{2-}$ range of 0.5 mM to 1.0 mM however is not clear. In the case of $SeO_4{}^{2-}$, the lower concentrations (*e.g.* 0.1 mM) appear to have a stronger effect then the higher concentrations. It is very likely therefore that selenium plays an important role in the geochemical mobility of fluoride in soils and in the groundwater. Selenium is known to affect the health of human beings and animals while fluoride is an important chemical species detrimental to dental health when either deficient or found in excessive levels. The interactions of the selenium species and fluoride on clay will therefore govern their bioavailability and hence their relative importance in health.

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