Dissolution of fluoride in groundwater: A water-rock interaction study

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Dissolution of fluoride in groundwater: a water-rock interaction study

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Abstract Fluoride-rich groundwater is well known in granite aquifers in India and the world. Although its presence is necessary, chances of health risk become high if the fluoride concentration is more than the permissible limit of 1.5 mg/l (World Health Organization, WHO) in drinking water. Fluoride mainly occurs in groundwater as a natural constituent. Results of a laboratory study on water-rock interaction at normal temperature, pressure and different chemical conditions indicate that the specific conductivity, pH, Ca and HCO_3 are important chemical parameters for the dissolution of fluoride to groundwater from fluoride-rich minerals (e.g., fluorite). Experimental results indicate that an alkaline medium (pH=7.6 to 8.6), high HCO_3 concentration (ranging from 350–450 mg/l), and moderate specific conductivity (ranging from 750–1,750 μS/cm) are favourable for fluoride dissolution. No significant correlation existed between fluoride and $CaHCO_3$.

Keywords Fluoride · Water-rock interaction · Granite rocks · Weathering · Dissolution

Introduction

High fluoride concentration in groundwater is found in areas of bedrock containing fluoride minerals (Handa 1975; Wenzel and Blum 1992; Bardsen and others 1996). The subsurface rocks in an area control the zones in which weathering affects the host rocks in minerals (Perez and Sanz 1999). The fluorine element in fluorine-enriched minerals dissolves gradually in the groundwater, and becomes one of the main trace elements. In general, fluoride minerals are sparingly soluble in water. Free fluorine is unstable, and plays no part in toxicology because it reacts immediately to form fluoride compounds. The presence of dissolved fluoride is possible only under favourable physico-chemical conditions and when residence time is long enough (Kullenberg and Sen 1973; Handa 1975). Among all the fluoride-rich minerals, fluorite is most abundant and occurs in almost all rocks and detrital minerals. Chemically, fluoride and OH ions are negatively charged and also have almost similar ionic sizes. Hence, during the chemical reaction, fluoride can easily replace OH ions in many rocks forming minerals. In the weathering process, hydrolysis, dissociation and dissolution occur with time. For example, if the groundwater is rich in HCO_3, the following type of reaction takes place during the water-mineral (fluorite) interaction:

$$CaF_2 + Na_2CO_3 \rightarrow CaCO_3 + 2F + 2Na$$

$$CaF_2 + 2NaHCO_3 \rightarrow CaCO_3 + 2Na + 2F + H_2O + CO_2$$

In the above reactions, the $NaHCO_3$-rich water in a weathered rock formation accelerates the dissolution of CaF_2 to release fluoride into the groundwater with time. In these reactions, the concentration of dissolved ionic species and the pH of the water play an important part. Minerals rich in calcite ($CaCO_3$) also favour the dissociation of fluoride from fluoride-rich minerals, and this can be shown as:

$$CaCO_3 + H + 2F \rightarrow CaF_2 + HCO_3$$

$$CaF_2 \rightarrow Ca + 2F$$

$$K = \{a(HCO_3)\}/\{a(H)^* a(F)\}$$

where K is an equilibrium constant, and a is the activity. It is evident that, if the pH is constant, the activity of fluoride is directly proportional to HCO_3. This relationship is independent of Ca because of the low solubility product of CaF_2.

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Sample collection and analysis

For the water-rock interaction study, a sample was collected from a 14.5-m-deep well located at Patabellam village in the Krishna District of Andhra Pradesh (Fig. 1). This village, along with the surrounding villages within an area of 135 km^2, is found in a zone of known fluoride-rich groundwater (Rao 1976). The water sample from the well was collected in April 1999 (pre-monsoon period, with a low groundwater level), and it was analyzed the same month using chemical methods in Brown and others (1973), Greenberg and others (1992), and Chmilenko and others (1998). The result of the chemical analysis is given in Table 1. Analysis shows that the water is mildly alkaline with high bicarbonate (350 mg/l) and high fluoride (5.5 mg/l) concentrations. This water can thus be classified as Na-Ca-HCO_3-Cl. The fluoride concentration is also high in terms of drinking water standards (USPHS 1987), exceeding the permissible limit of 1.5 mg/l for drinking water (WHO 1984).

The geological formation of this region is mainly granite and gneisses covered with black clayey soil. A water-rock interaction study was carried out near the well at Patabellum village. A sample of rock was collected from an exposure close to the well. The rock was crushed, powdered and messed. Subsamples were used for chemical analysis and the water-rock interaction study. Results of the chemical study are given in Table 2.

The analyses show that fluorite content is high (0.92%) in the rock sample.

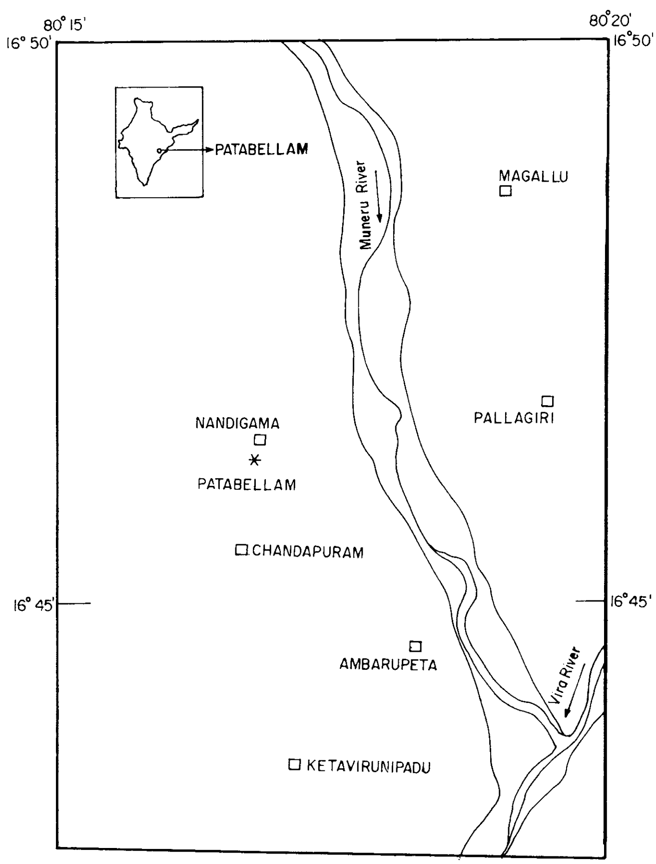

Fig. 1
Geographical location of the sample collection

Table 1
Result of chemical analysis of water sample (specific conductivity at 28 °C=1,540 μS/cm; pH=7.8)

Element	Concentration (mg/l)
Na	245
K	10
Ca	106
Mg	28
Cl	155
HCO_3	350
SO_4	85
F	5.5
TDS	1,050

Table 2
Result of chemical analysis of rock sample

Element	Content (%)
SiO_2	71.50
TiO_2	0.28
Al_2O_2	10.80
Fe_2O_3	3.2
FeO	1.5
MgO	3.15
CaO	2.5
Na_2O	4.05
K_2O	2.3
P_2O_5	0.05
CaF_2	0.92

Water-rock interaction experiment

An experimental study in four different steps was performed in the laboratory on a portion of the rock sampled under normal temperature and pressure conditions.

In a first case (case 1, Table 3), water of pH=7.6 and conductivity=1,500 μS/cm was used for interaction over various time intervals (2, 7, 15, 30, 60 and 90 days). Subsequently, the water was collected, filtered through 0.45-μm resin, and analysed for F, Ca, HCO_3, pH and specific conductivity. The results of these chemical analyses indicate a much faster dissolution of fluoride in water but no correlation between fluoride and the other chemical parameters.

In a second case (case 2, Table 3), water of conductivity=1,500 μS/cm and pH=6.6 were used. Compared with case 1, the results show that there is less dissolution of F and HCO_3, and fluoride is not proportional to HCO_3 or Ca.

In a third case (case 3, Table 3), the specific conductivity of the water was 750 μS/cm and the pH was changed to 7.6. A similar experiment was then carried out. In this case, the

Table 3
Water-rock interaction experimental results

Experiment time in days	pH		Specific conductivity		Ca		HCO_3		F	
	i	ii	i	ii	i	ii	i	ii	i	ii
Case 1 (specific conductivity=1,500 μS/cm, pH=7.6, 28 °C)										
2	7.6	7.7	1550	1568	120	124	280	295	1.0	1.2
7	7.6	7.9	1550	1592	120	136	280	327	1.0	2.1
15	7.6	8.2	1550	1660	120	145	280	382	1.0	2.6
30	7.6	8.3	1550	1688	120	152	280	405	1.0	3.3
60	7.6	8.4	1550	1693	120	158	280	426	1.0	3.8
90	7.6	8.6	1550	1732	120	165	280	442	1.0	4.6
Case 2 (specific conductivity=1,500 μS/cm, pH=6.6, 28 °C)										
2	6.6	6.7	1550	1556	120	122	280	288	1.0	1.1
7	6.6	6.8	1550	1564	120	128	280	302	1.0	1.8
15	6.6	6.8	1550	1572	120	134	280	312	1.0	1.9
30	6.6	7.4	1550	1582	120	142	280	405	1.0	2.2
60	6.6	7.8	1550	1605	120	154	280	412	1.0	2.2
Case 3 (specific conductivity=750 μS/cm, pH=7.6, 28 °C)										
2	7.6	7.6	750	752	60	61	190	194	1.0	1.1
7	7.6	7.8	750	764	60	69	190	201	1.0	1.5
15	7.6	8.2	750	772	60	73	190	212	1.0	2.0
30	7.6	8.3	750	785	60	80	190	222	1.0	2.2
60	7.6	8.4	750	795	60	84	190	235	1.0	2.3
90	7.6	8.4	750	802	60	93	190	246	1.0	2.4
Case 4 (specific conductivity=750 μS/cm, pH=6.6, 28 °C)										
2	6.6	6.6	750	755	60	61	190	192	1.0	1.1
7	6.6	6.7	750	762	60	63	190	197	1.0	1.3
15	6.6	7.2	750	780	60	66	190	203	1.0	1.4
30	6.6	7.6	750	792	60	70	190	215	1.0	1.5
60	6.6	7.9	750	832	60	85	190	245	1.0	1.6
90	6.6	8.4	750	872	60	97	190	256	1.0	1.6

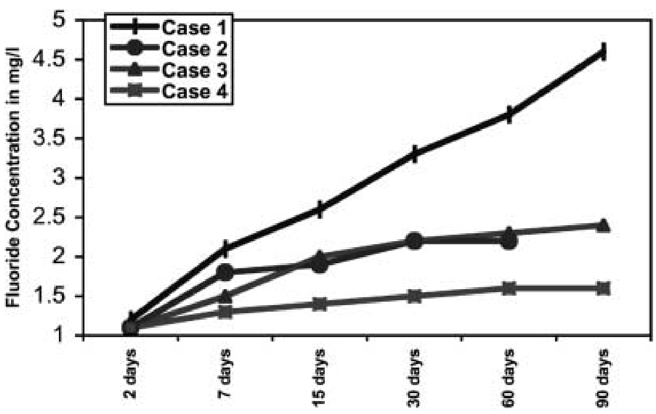

Fig. 2
Water-rock interaction experiment: increase in fluoride concentration with time

results show a slow dissolution at the beginning of interaction, which gradually became even slower thereafter. In a fourth case (case 4, Table 3), the experiment was performed with specific conductivity=750 μS/cm and pH=6.6. The results indicate that the fluoride dissolution was relatively slow throughout the process, and that it became stable between days 60 and 90 at the end of the experiment. Figure 2 depicts the change in fluoride concentration for cases 1 to 4 in the water-rock interaction experiment.

Conclusions

Aqueous ionic species and concentrations, as well as their interactions with fluoride-enriched minerals and residence time are important in controlling the fluoride dissociation process. Alkaline conditions (pH ranging between 7.6 and 8.6) and moderate specific conductivity (ranging from 750–1,750 μS/cm) are favourable for fluoride dissolution from fluorite to water. No significant correlation exists between fluoride and $CaHCO_3$.

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