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Geochemistry and role of calcium for the availability of fluoride in the groundwater of Pappireddipatti Block, Dharmapuri district

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ABSTRACT

Water is the most precious gift of nature for sustaining life and environment. The most unusual characteristic of water is its ability to dissolve a greater range of substances than any other liquid. The slow percolation of water through the ground results in prolonged contact of water with minerals in the soil and bedrock. India is one of the richest countries in the world for occurring fluoride bearing minerals. The study area is enriched with a variety of fluoride bearing minerals and groundwater is used as the major source for drinking and irrigation purposes. The geochemistry of the study area is very much favorable for the release of Fluoride ion into the groundwater. Many locations of the study area bear fluoride concentrations moderately higher than the WHO permissible limit. The higher pH, enhanced alkalinity, carbonate values and low calcium with respect to WHO standard indicates the fluoride leaching mechanism and also explain the rock-water interaction. Large numbers of people living in this region were affected by fluorosis.

Keywords: Groundwater, minerals, Fluoride, Fluorosis.

INDRODUCTION

Fluorine is the 13th most abundant element in the earth crust (625 mg/Kg) (Manoucher Amini et al, 2007) . It is the most reactive non-metal and more electronegative element. Therefore almost never occurs in nature in its elemental state. Fluorine is probably an essential element for animals and humans. Low concentration provides protection against dental caries, especially in children. Minimum concentration of fluoride in drinking water required to produce protective effects is approximately 0.5 mg/L. Fluoride is present in the form of naturally occurring minerals such as fluorite (CaF_2), cryolite (Na_3AlF_6), topaz, tourmaline, muscovite, biotite, villianmit (Handa 1975, Pickering 1985, msonda et al 2007). The occurrence of fluoride in ground water is due to the leaching and weathering of fluorite, apatite and mica etc., (S.Mukherjee et al 2011). The rock types are dominant with high fluoride concentration encircling the groundwater. The fluoride concentration in groundwater is found to be higher due to high alkalinity. Thus fluoride rich groundwater is often associated with low calcium content. The concentration of fluoride is controlled by Fluorite (CaF2).

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

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

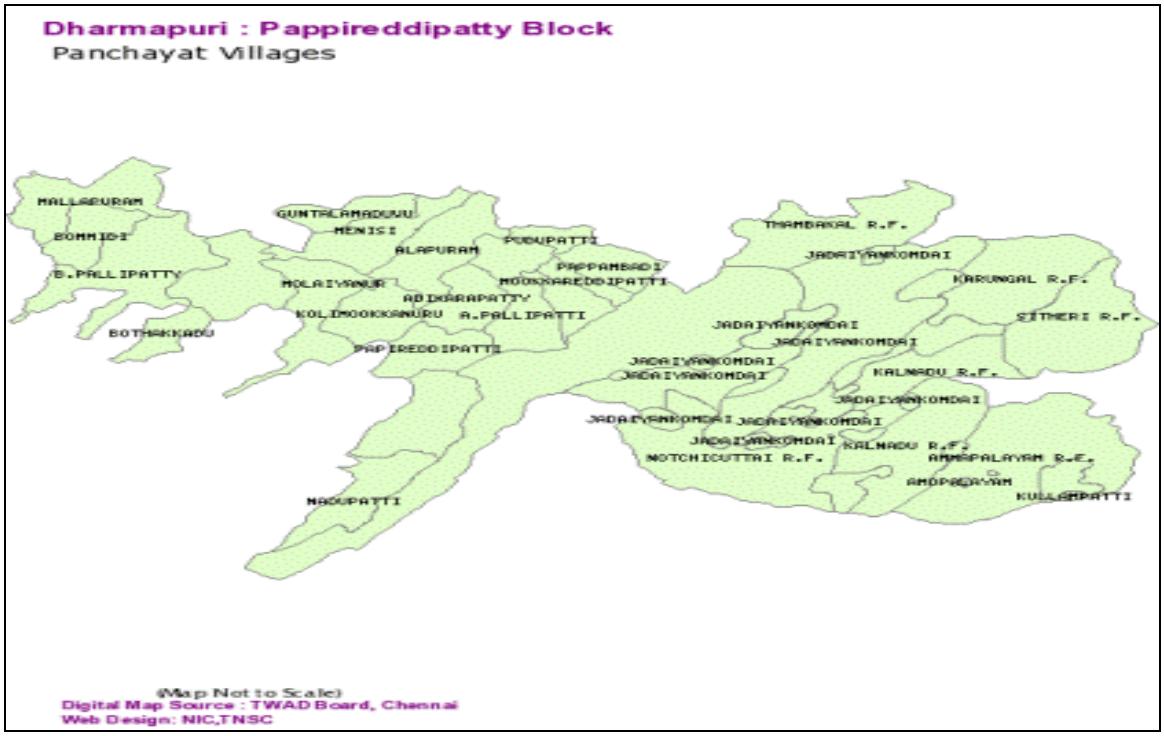
In the above reactions the $NaHCO_3$ rich water in a weathered rock formation accelerates the dissolution of CaF_2 to release fluoride into the ground water with time, so the concentration of dissolved ionic species and pH of the water play an important part for analyzing the fluoride geochemistry.

In the present study the occurrence, fluoride geochemistry and role of calcium for the availability of groundwater and its impacts in the groundwater of Pappireddipatti Block, Dharmapuri district were discussed.

MATERIALS AND METHODS

Profile of the study area:
Pappireddipatti Block, Dharmapuri is district located at 11 45' to 12 53' N and 77 13' to 77 45' E. The district receives an average annual rainfall from 760 to 910 mm. Agriculture is the back bone of this region. Geologically the district is underlain by the formations of crystalline rocks comprising charnockites, gneisses and associated rocks. Groundwater is mainly used for drinking and irrigation purposes.

Fig: 1 -Map highlighting the study area



Sample Collection:
A total of 23 samples were collected from hand pump and Bore well at different locations of the entire Pappireddipatti Block during the summer season of May and June 2012. This period was selected to assess the contamination due to low dilution and the accumulation of ions. The water samples were collected in pre-cleaned, sterilized polythene bottles of 2 Lt Capacity.

Methodology:
The samples were analyzed to assess various physico-chemical parameters according to APHA (2007). pH and electrical conductivity of the groundwater samples were measured by using potable pH meter (Systronics 335) and EC meter (Systronics 304) respectively. Total alkalinity and total hardness were measured by titrimetric method using standard sulphuric acid and standard EDTA (Ethylene Diamine Tetra Acetic acid) solutions respectively. Phosphate was measured by Gravimetric method. The cations sodium and potassium were analyzed by using flame photo meter (Systronics 130). Calcium was assessed using titrimetric method. Chloride was determined by using argentometric method. The fluoride concentrations were measured by using Spectrophotometer (systronics model

104). The sodium fluoride was used to prepare the standard solutions and the SPADNS solution was used for the colour development. Analytical grade chemicals were used throughout the study without further purification. To prepare all reagents and calibration standards, double distilled water was used.

Table-I: Physico-Chemical characterization of ground water in Pappireddipatti Block.

Sample Numbers/ Parameters	pH	EC	TDS	ALKALINITY	CO_3^{2-}	HCO_3^-	Hardness	Ca^{2+}	Mg^{2+}	Cl^-	Na^+	K^+	F^-
1	6.9	1160	661	504	42	462	441	71	89.9	160	25	0.83	2.o
2	7.1	1200	684	487	56	421	313	31.7	68.3	75	30	0.71	2.8
3	7.3	2100	1197	570	42	528	494	107	94	357	52	2.02	1
4	7	2400	1368	431	35	396	566	133	105	365	211	33.2	1
5	8	540	308	301	24	277	275	36.3	58.5	105	16	0.59	10
6	7.3	930	530	231	22	209	328	58.9	65.4	175	28	1.19	8
7	7.2	3300	1881	480	46	434	890	96.7	193	735	72	2.49	10
8	7	3100	1767	534	60	474	592	104	119	165	333	56.7	8
9	7.1	2500	1425	443	10	433	664	136	128	507	238	38.2	11
10	7.8	890	507	450	50	400	279	40.8	57.9	162	36	0.35	14
11	7.2	1290	735	319	22	297	418	66.5	85.4	262	89	5.11	11
12	7.1	2200	1254	525	30	495	607	87.6	126	400	70	4.28	14
13	7.1	1210	690	502	24	478	528	80.1	109	122	22	0.47	14
14	7.1	1280	730	410	32	378	460	83.1	91.6	355	153	12.6	11
15	7.2	860	490	305	55	250	426	92.2	81.1	170	21	2.9	14
16	7	700	399	266	70	196	268	37.8	55.9	112	40	1.66	14
17	7.4	3400	1938	450	46	404	943	139	195	975	82	6.64	14
18	6.9	2400	1368	359	20	339	66	115	139	562	165	24.9	14
19	6.8	4300	2451	343	30	313	520	305	52.2	1297	77	5.35	14
20	6.9	1500	855	397	24	373	558	131	104	422	81	6.3	8.8
21	7.3	2300	1311	464	76	388	845	119	176	730	35	1.66	13
22	6.9	940	536	341	22	319	354	48.4	74.3	260	32	0.48	14
23	7.2	1680	958	698	45	653	347	33.2	76.2	137	37	0.83	14

**All the parameters are expressed in mg/L except pH and EC in µS/cm.*

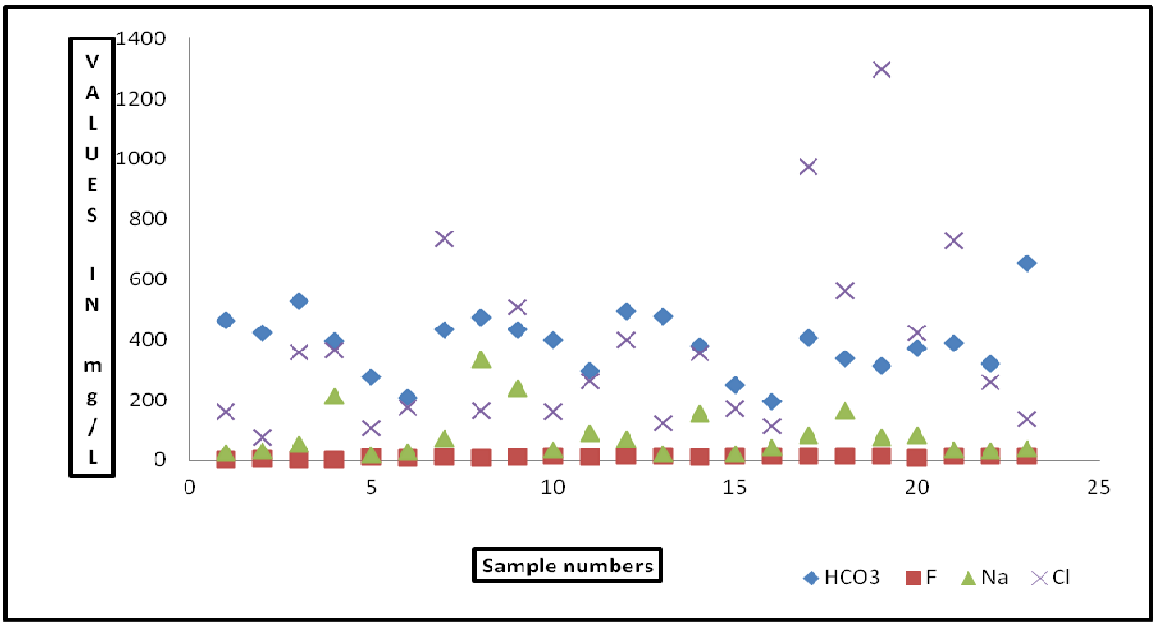
RESULTS AND DISCUSSION

Various physicochemical parameters were analyzed and tabulated as shown in table-I. In general majority of the ground water samples were found to be free from colour, odour and turbidity except a few samples.

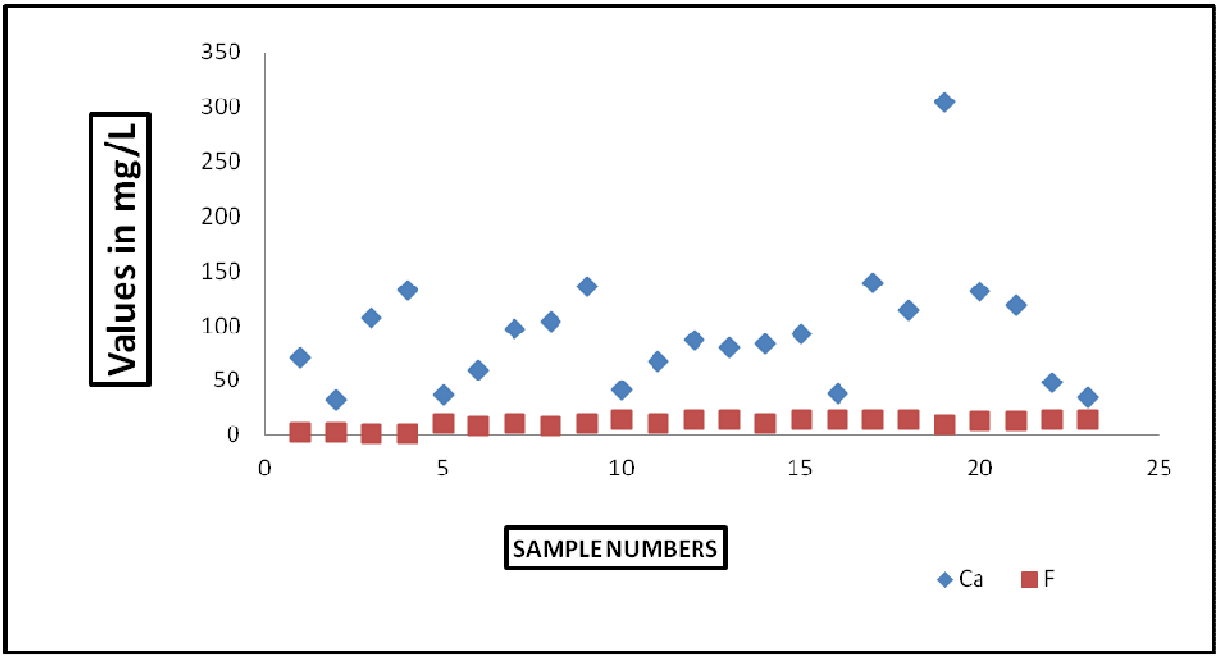
In Many stations the pH values were greater than 7.0, which indicate that the ground water samples are alkaline in nature .The WHO acceptable limit for alkalinity in drinking water is 200 mg/L. In our study all the groundwater samples having alkalinity values more than the permissible limit. The total hardness values were found within the permissible limit except a five locations. The calcium and magnesium values were found above the permissible limit in the ranges from 83.1 mg/L to 305.22 mg/L in 14 locations and the remaining locations the values were found to be within the permissible limit. The permissible limit of magnesium is 30 mg/L (BIS), in our study all the groundwater samples show the magnesium value within the permissible limit. The desirable level of chloride set by WHO is 200 mg/L .The range of chloride observed in our study ranges from 75-1297 mg/L in ten locations the chloride values were found to be within the permissible limit. A high chloride concentration in water affects the kidney tissues, mainly for the young children.

Sample locations:
1-Manjavadi, 2-Nadupatti, 3-Samiyapuram, 4-Pappireddipatti, 5-Vengadasamuthiram, 6-Pooniyanoor, 7-Devarajapuram, 8-Paiernatham-I, 9-Pairenatham-ii, 10-Jagalahalli, 11-Kumparahalli, 12-Vasigoundanoor, 13-Kathiripuram, 14-Kundalamedu, 15-Irularcolony, 16-Poothanatham, 17-Gopalapuram, 18-Paripatti, 19-Mookareddipatti, 20-Kottamedu, 21-Alamelupuram, 22-Kallthupatti, 23-Kompoor.

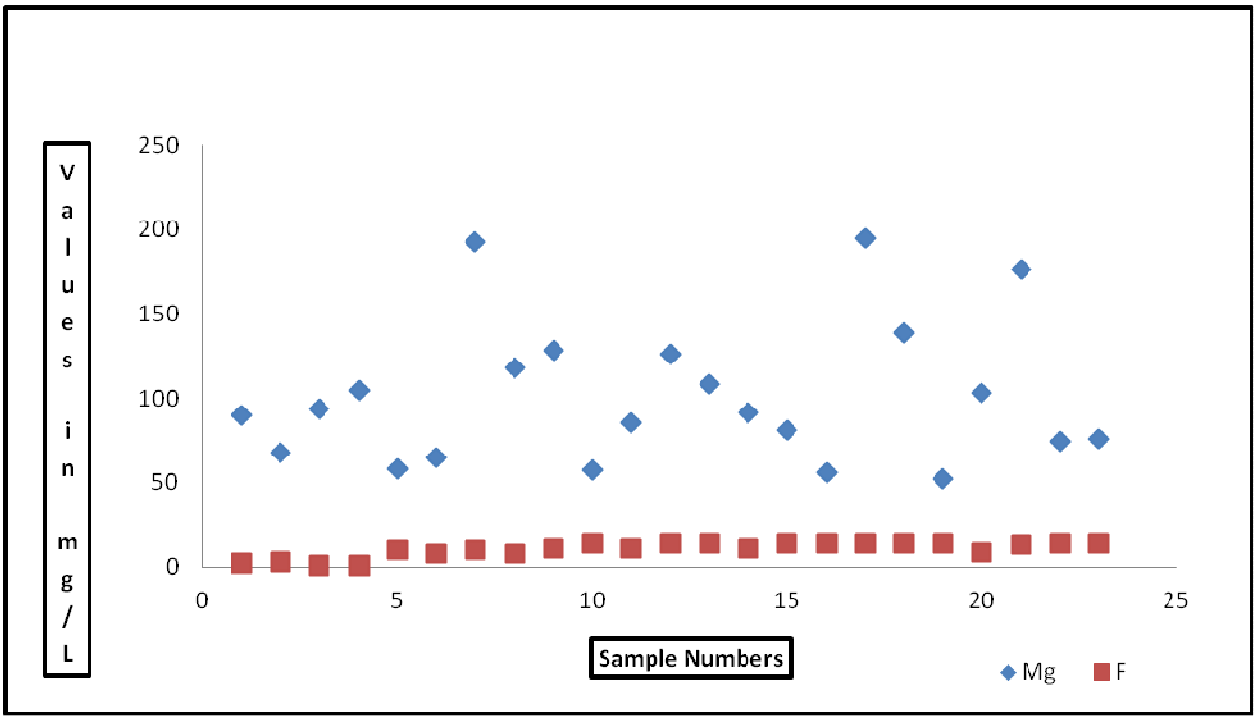
Graph-1- Relationship between Bicarbonate, sodium, Chloride and Fluoride



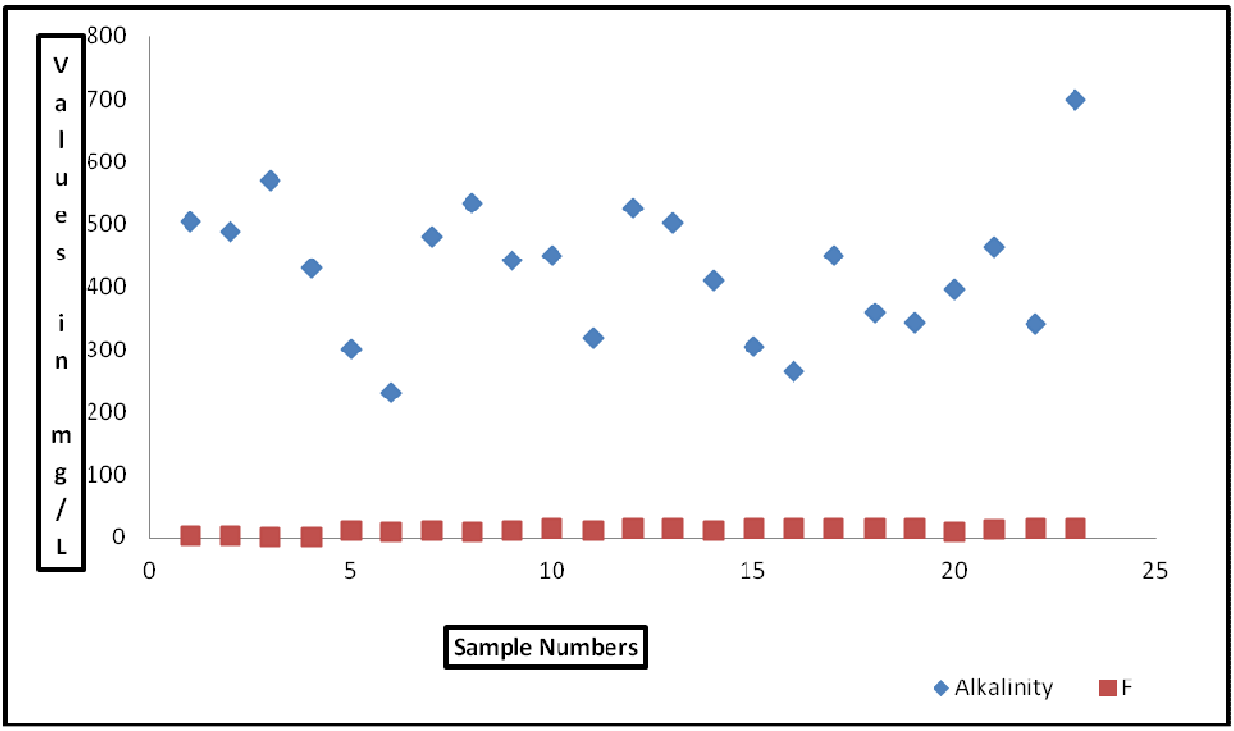
Graph: 2-Relationship between calcium and Fluoride



Graph:3 -Relationship between Magnesium and Fluoride



Graph: 4 -Relationship between alkalinity and Fluoride



Fluoride:

One of the major sources of fluoride in aquatic system is the weathering of fluorite although fluoroapatite, mica, etc., have hydro geochemical effects on the concentration of fluorite and calcite provides a natural control on water composition, such that calcium, fluoride and carbonate activities are interdependent. (N.Kundu et al: 2001).In our study nearly 21 samples having the fluoride concentration above the permissible limit when compared to the WHO permissible limit. From the *Graph: 1* it is observed that the Na, Cl and HCO_3 show positive relationship with fluoride, whereas Ca and Mg show a negative relationship with fluoride from the Graph*: 2 and: 3* respectively .High fluoride and low Ca and Mg in water may be due to the prior precipitation of $CaCO_3$ from water and only limited incorporation of F^- in the $CaCO_3$ structure (N.Kundu et al: 2001), so that there is always a net balance of fluoride in solution. In our study some locations the calcium concentrations show negative relationship with fluoride (Graph*: 2*), it indicates the concentration of fluoride is controlled by CaF_2. The fluoride inn groundwater appears to be controlled by the distribution of Ca^{2+} and the geochemistry of the study area fluoride was found to be inversely related to calcium and positively related to Na^+.(Guptha c.s et al, 2006). A higher value of Fluoride with alkalinity (*Figure: 5*) indicates the carbonate rocks are in contact with the fluoride bearing minerals in these locations. The ground water in the area is brackish and highly contaminated by fluoride. The granitic rocks are present in this area contain large amount of fluoride bearing minerals and it leached out and dissolve in ground water. In our study it was found that so many locations were showed higher concentration of fluoride compares to the WHO permissible limit. Geochemical processes such as ion-exchange, dissolution and weathering are responsible for fluoride contribution in ground water. The release of fluoride to groundwater is dependent on chemical and physical processes that take place between the groundwater and its geological environment. Fluorite is the predominant mineral that controls the dissolved fluoride concentration in the groundwater (Edmund S.M et al, 2005, Ayoob.S et al, 2006). Thus fluoride rich groundwater are often associated with low calcium concentrations, this is associated with rocks with low calcium content or high pH conditions where sodium bi carbonate dominates the groundwater composition apart from the groundwater chemistry. Hydrological properties as well as climate conditions and soil conditions have an influence on fluoride concentration. Hence the spatial and temporal heterogeneities of fluoride concentration in groundwater are particularly large.

CONCLUSION

Fluoride is often called two edged sword, fluoride in small dosage has remarkable influence in the dental system by inhibiting dental caries, and while in higher dosage cause severe dental and skeletal fluorosis. Mainly Pappireddipatti and its surrounding villages present a higher amount of fluoride concentration in ground water depends upon its geochemical formations. So the public using ground water with proper treatment is safe for their better health.

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