International Conference "Water, Environment, Energy and Society" (WEES–2009)
New Delhi, 12–16 January 2009

Identification of Geogenic Sources of Fluoride in Hard Rock Regions: A Case Study from Southern India

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ABSTRACT: The problem of fluoride in drinking water is a major health issue in many countries. In Hard Rock (granite, gneiss) aquifers of southern India, many drinking water supplies present fluoride levels higher than threshold values (1.5 mg/L, according to WHO), beyond which, population gets affected by dental and skeletal fluorosis. Fluorine is mainly found in aqueous solution (fluoride) or in solid salt (fluorite). This fluorine is present in some minerals (micas, amphiboles) in granites, gneiss and pegmatites, and it is released in solution due to weathering of these primary minerals. In contrast, kaolinite is a sink for fluoride. Fluoride is common in semi-arid climate with crystalline igneous rocks and alkaline soils. The objective of this research project is to identify the main sources of geogenic fluoride in Hard Rock regions typical of southern India. To do so, both fresh and weathered rock samples were collected in an experimental watershed near Hyderabad (Andhra Pradesh) where high fluoride groundwater concentrations have been observed in some locations. The watershed is composed by Archean Biotite Granite (BG) and Leucocratic Granite (LG) injected by some quartz reefs, dolerite dykes and pegmatites (BGP). Rock samples were taken from each of these main lithologies. Petrographic examination and modal analysis were first carried out and then, selected sections were chosen for detailed electron probe analysis to test the chemical composition of apatite, biotite, epidote, sphene, chlorite, and allanite minerals. In addition some weathering processes in relation with fluoride release have been identified: chloritzation of the biotite and metamictization of allanite. Another process is also inferred and may act as fluorine sink: the formation of REE fluoro-complex in allanite only in presence of biotite. The results give the chemical composition of different minerals for each rock type. Based on the results of more than 250 probe analyses, it is found that the main fluoride-bearing minerals are in decreasing importance: apatite, sphene, biotite, allanite, epidote, and chlorite. However, according to the proportion of these minerals in the rock, the major contributors of geogenic fluoride are biotite and epidote for BG and BGP, and biotite allanite and epidote for LG.

Keywords: Fluorosis, Geogenic Sources, Granites, Southern India, Hard Rocks.

INTRODUCTION

The problem of high fluoride concentration in groundwater regime has now become one of the most important toxicological and geo-environmental issues in India. Ingestion of higher fluoride by any means viz., air, water causes severe affects on human and animal physiology. Dental and skeletal fluorosis are among the lethal impacts on the human. Several researchers viz., Handa, 1975; Apambire *et al.*, 1997; Saxena and Ahmed, 2001 worked on fluoride occurrence and distribution in groundwater. The threshold value limit for fluoride is 1.5 mg/l, as prescribed by the WHO standard beyond which, population gets affected by dental and skeletal fluorosis. The origin of fluoride in groundwater can be related to both natural and anthropogenic sources. Fluorides are found at significant levels in a wide variety of minerals, including fluorite, rock phosphate, cryolite, apatite, mica, hornblende and others. The degree of weathering and the leachable F^- in a terrain is more important in deciding F^- content in the water rather than the mere presence of F^- bearing minerals in the bulk rocks/soils (Ramesam & Rajagopalan, 1985).

The most common alteration product of the biotite is chlorite (Veblen, 1983). Allanite is the rAre Earth

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Element (REE) rich epidote species and could act differently, if present in association with biotite. In India, 17 states of the country reached to alarming stage of fluorosis (Susheela, 2003). Alarming stage means population of more than 70% of districts from these states are affected by dental or skeletal fluorosis. The fluorosis disease caused due the higher fluoride levels in groundwater (>1.5 ppm). Among various reported states Rajasthan, Andra Pradesh, Orissa, in parts of Uttar pradesh, Karnataka, Tamil Nadu, Madha Pradesh, Mahasrastra and Bihar belong to hard rock terrain, dominantly by granites, gneisses, schists (Susheela, 2003, Saxena & Ahmed, 2001). In some case, fluorite (CaF_2) can be the principal bearer of fluoride and reported in granite, granitic gneiss and pegmatite (Ramamohan Rao *et al.*, 1993). In the present study, authors attempt to understand identification of geogenic sources of fluoride and the probable release process.

ABOUT STUDY AREA

The Maheshwaram pilot watershed (Figure 1), 53 km² in area, is located 35 km south of Hyderabad, India. The area is characterized by relatively flat topography with altitudes between 670 and 590 m above mean sea level and the absence of perennial streams. The region experiences a semi-arid climate controlled by the periodicity of the monsoon. Mean annual precipitation is about 750 mm, of which more than 90% falls during the Monsoon season. The mean annual temperature is 26°C; however in summer the daily maximum temperature approaches 45°C.

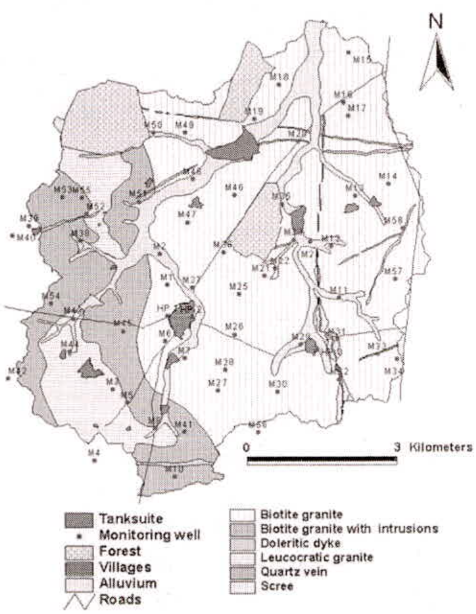

Fig. 1: Geological map of the study area with observation borewells

GEOLOGICAL SETTING OF STUDY AREA

Crystalline rocks of Archean age, comprising of gray and pink granites cover a major portion of the study area. The granites have been intruded by number of dolerite dykes and quartz veins at places. Recent alluvia occur along the stream courses. The granite is composed mainly of gray and pink feldspar belbs along with quartz grains in a coarser variety; where as the fine grained variety is composed of a uniform distributed mosaic of feldspar, quartz and biotite. The granites are transversed by a number of joint sets as observed on surface exposure and in the dug wells. Red silty soil covers the whole watershed in general. Hard and massive rocks are mostly exposed in the southern part while deep weathered zones are observed in the central and northern part of the watershed.

METHODOLOGY AND ANALYTICAL METHODS

Total 150 groundwater samples were collected in year 2006. The fluoride analysis was carried out by Hanna Instrument-High range ion-specific meter (HI-93739). The instrument works on SPADNS method (Banerjee, 1975). The instrument has a capability to measure the fluoride content in the water from 0–20 mg/l with an accuracy of ±0.5 mg/l to ±3% of the reading.

Total 50 representative specimen granite samples covering the total catchment were collected for study. 29 polished thin sections were prepared and petrographic examined, out of which 10 thin sections were selected for modal analysis. Modal analysis which is quantitative recording of mineral content is based on the visual estimation chart. Apart from the modal analysis, five thin sections, representative of apatite, biotite, chlorite and allanite grains were chosen for detailed analysis. The different mineral locations have been selected from these minerals, were based on fresh and altered state of minerals.

Mineral compositions were analysed, using a CAMEBAX SX–50 Electron Probe microanalysis (EPMA), at BRGM, Orléans, France. The microprobe is equipped with four Wavelength-Dispersion Spectrometers (WDS) and an Energy-Dispersion (EDS) attachment. Operating condition of the Microprobe was 15 keV accelerating voltage, 12 nA beam current, maximum of 10-s counting interval on peak and 5-s on the background. For the fluoride analysis natural topaz for F^-(0.2065%) was used as a standard. The analysis was employed with PAP correction procedure (Pouchou & Pichoir 1985). X-ray lines and background offsets were selected to minimize interferences and their correction (Roeder 1985).

RESULTS AND DISCUSSION

Results based on the ground water analysis, it has been found that fluorine range varies between 0.3 to 4.67 mg/l. Groundwater which belongs to BG rock shows fluoride variation from 0.40 to 4.67 mg/l while LG rock varies from 0.89 to 1.36 mg/l.

The petrography results of the catchment include quartz, K-feldspar (microcline), plagioclase, biotite and chlorite as major minerals while epidote, sphene, allanite, apatite and zircon are found as accessory minerals. Opaque inclusions of magnetite and at places REE Fluoro-complexes have been observed at places. Fine grained quartz crystals in the coarse grained matrix have been recognized, indicating the presence of recrystallization process and majority of the biotite is partially to completely chloritized. Elongated to sub-spherical sphenes, embedded in partially to completely chloritized biotites were observed at places. Abundance of tiny scattered crystals of apatite were observed inside the alkali feldspar. Fine to medium grained isolated crystals of apatite were found commonly in fractures and opaque minerals including magnetite, in association with biotite and allanite. Dislocated biotite flakes in the fractures and elongated epidote crystals in chloritized biotite have been observed at number of places. Modal analysis result shows that BG dominantly covers potash feldspar (32%) followed by the plagioclase (28%), quartz (26%), biotite (7%). An approximate estimation for the other accessory minerals viz., epidote (≈2%), oxides (≈2%), chlorite (≈1%), apatite and allanite (<1%) has been carried out. LG consists 46% potash feldspar, plagioclase (18%), quartz (30%), chlorite (≈2.5%), epidote (≈2%), both Fe-oxides & allanite (≈1%) and apatite & other minerals (<1%). Figure 2 shows diagrammatic representation of different minerals from BG and LG of the selected watershed.

Based on more than 250 micro-probe analysis, it is found that the main fluoride-bearing minerals are in decreasing importance: apatite, sphene, biotite, allanite, epidote and chlorite. Considering the proportion of these minerals in the rock, it has been proposed that the major contributors of geogenic fluoride are biotite, and epidote for BGP and BGP with pegmatite intrusions, while biotite, allanite and epidote for LG. In addition to these minerals, some complex mineral phases with very high fluorine content have been recognised viz. REE fluoro-complex.

It is found that fresh apatite crystals have higher fluoride content (average, 3.5 wt %) compared to semi-weathered (average, 2.76 wt %). As apatite and sphene are poor soluble minerals and their less abundant, thus insignificant in the present context. Optical microscopy showed biotite to be light to medium brown, with green alteration. These phases are large enough to determine chemical compositions of the separate phases with an electron microprobe. Average amount of fluoride in biotite and chlorite is 1.08 and 0.16 wt % respectively. Veblen (1983) has already shown that the most common alteration product of the biotite is chlorite. Negative linear correlation of aluminium and fluoride with a correlation coefficient of 0.80 has been found which also supports the possible chloritization process for the release of the fluoride from biotite. As the chloritization of biotite continues, decrease in fluoride have been observed with the increase of aluminium.

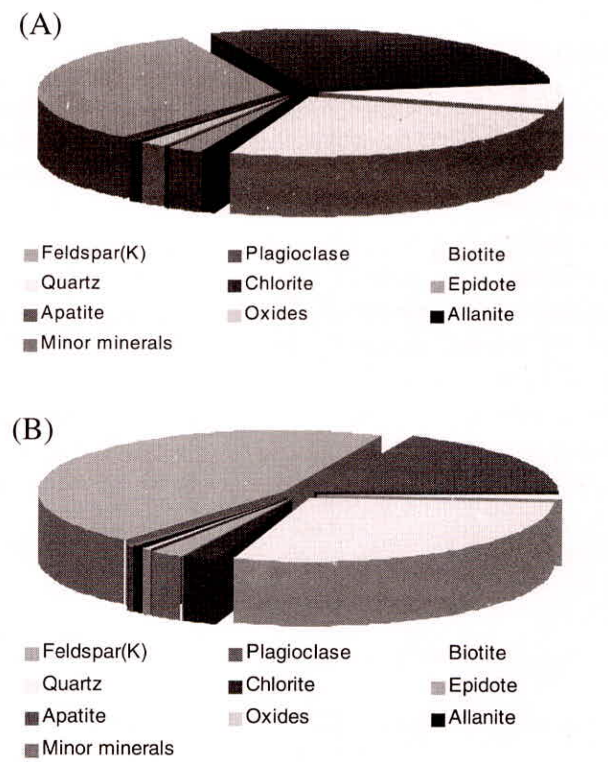

Fig. 2: Mineral proportions of (A) biotite granite: BG and (B) leucocratic granite: LG

Allanite is the REE rich epidote, commonly found in metamict state in these granites. The metamict process leads to the destruction of the crystalline structure due to the bombardment of the alpha particles that result from the disintegration of radioactive elements and decay products in the mineral. Further, the action of the meteoric water accelerates alteration reactions. The REE rich mineral in the vicinity of biotitic granite makes the system relatively more complex. Allanite is the REE rich epidote, commonly found in metamict state in these granites. The metamict process leads to the destruction of the crystalline structure due to the bombardment of the alpha particles that result from the disintegration of radioactive elements and decay products in the mineral. Further, the action of the meteoric water accelerates alteration reactions. The REE rich mineral in the vicinity of biotitic granite makes the system relatively more complex. The alteration of biotite to chlorite and or kaolinite causes release of fluorine, which couples with allanite and results formation of REE fluoro-complex. From EPMA investigation fluoride in some clay material (0.1 to 0.4 mg/g) also have been observed which is could be result of adsorption process. The variation of the fluoride in the metamict allanite porphyroblast shows fluoride heterogeneity due to the removal at one place and local enrichment at others. This could be due to the higher affinity of fluorine with rare earth elements.

CONCLUSIONS

It is therefore, concluded that alteration of biotite and fluoro-apatite are prime responsible processes giving rise to geogenic release of fluoride in such granitic hard rock aquifer. The alteration of biotite givies rise to kaolinite through intemediate stage of chlorite. This identification may be used to delineate the zones of geogenic and anthropogenic contamination and thus may be used for planning for drinking water supply as well as containing the anthropogenic causes.

ACKNOWLEDGEMENTS

The authors wish to thank the Director, NGRI, for permission to publish the paper. This study was carried out at the IFCGR (NGRI- BRGM). First author would like to thank the French Embassy in India, MAE for giving an opportunity to work at BRGM, Orléans, France & Financial assistance was provided by the MAE and CSIR-New Delhi. Also the authors are thankful to the Monique Tegyey, C. Gilles and R.Wyns, Senior Scientists from BRGM, France for assistance during analysis and useful discussion.

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