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ORIGINAL ARTICLE

The levels of fluorine in the sediments of the aquifer and their significance for fluorosis in coastal region of Laizhou Bay, China

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Abstract The levels of fluorine in sediment cores obtained from Changyi County (PZ core) and Laizhou County (TS core) are used to discuss the fluorine sources in groundwater and its enrichment dynamics. The sediments in the aquifer are mainly constituted of granite gravels. The levels of fluorine in the PZ and TS cores range from 130 to 468 mg/kg, 139–528 mg/kg, with average values of 324, 348 mg/kg, respectively, which show relatively lower levels than the national average of fluorine in the soil or sediment. Thus, the fluorosis in this area should not be attributed to the levels of fluorine in sediments. The average fluorine concentrations in the aquifer from top to bottom are 154, 139, 200, 222 mg/kg for the TS core, and 154, 130, 266, 272 mg/kg for the PZ core, respectively, which are the lowest of the cores and extremely lower levels than the fresh granites. Such a fact indicates that a vast amount of fluorine has been leached into the groundwater. Moreover, the fluorine leachability is estimated to be approximately 70 %, although the previous documents showed fluorine contents of the granite surrounding Laizhou Bay were almost equal to or even lower than the average levels of fluorine in fresh granites. Meanwhile, a simulation experiment also reveals that fluorine release from rocks increases with the addition of seawater and brine water. Therefore, the seawater intrusion may potentially enhance the fluorine leachability, and should be an important dynamic of fluorine enrichment.

Keywords Fluorine contents · Sediment · Fluorosis · Laizhou Bay · Seawater intrusion

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Introduction

Fluorine is a widespread, chemical element in the geographical environment and of great importance for human health, particularly for the preservation of teeth and bones. However, excessive intake causes dental or skeletal disease, known as fluorosis (WHO 1984; Harrison Paul 2005). The development and occurrence of fluorosis originate from high fluorine content in the soil, air or water. Water is perhaps the major contributor (Chen et al. 2011, 2012). Fluoride concentrations in water and the health problems it causes have been the subject of numerous studies in recent years (Gaciri and Davies 1993; Apambire et al. 1997; Fantong et al. 2010).

Universal, water-drinking endemic fluorosis occurs in Laizhou Bay, an area in the northern, coastal region of Shandong Province, China. It is estimated that more than 640,000 people are suffering from dental or skeletal fluorosis because of long-term consumption of fluoride-contaminated water (Han 1997). Fluorine contamination of the water can reach more than 12 mg/L (Yun et al. 2005). Moreover, fluorosis has been on the rise and new areas have been appearing in recent years (Yun et al. 2005; Gao et al. 2007a).

The amount of naturally occurring fluorine in groundwater is governed principally by hydrogeology, climate, the composition of the host rock, depletion of groundwater table, anthropogenic activities such as the use of pesticides, phosphatic fertilizer, dumping industrial sewage and sludge and so on (Ramanaiah et al. 2006). However, the majority of fluoride is derived from rock minerals on the earth's surface, whereas other sources such as air, seawater, and human activities constitute a relatively small proportion (Fuge 1988; Lahermo et al. 1991). Therefore, the main source of fluorine in groundwater is considered to be the fluorine-bearing minerals such as fluorspar, cryolite, hydroxy apatite and fluorapatite in rocks (Farooqi et al. 2007) under prolonged exposure to water (Carrillo-Rivera et al. 2002).

In the areas affected by fluorosis in Laizhou Bay, many investigations have been made related to the levels of fluorine in water, epidemiology and the correlation of fluorine with some inorganic constituents (Yun et al. 2005; Li 2007). The scope of distribution and the health-related impacts of high fluorine groundwater in this area are well known. However, a bibliographic survey showed that no researches have detailed the fluoride source, genesis and the processes that induced fluorine enrichment so far in this area. Therefore, an investigation of the level of fluorine in the sediment of aquifer is necessary for the scientific management, sustainable use of groundwater and the prevention of fluorosis.

In this experiment, two drills were carried out to obtain two sediment cores in Laizhou County and Changyi County, respectively. These areas have serious problems with fluorosis. The levels of fluorine in the sediment of the aquifers were studied to determine the interactions between the water, rock or sediments, which is ultimately expected to observe the peculiar geochemical features in the aquifer. The present study was conducted to: (1) reveal the characteristics of sediments in the aquifer and the geological setting of fluorine enrichment in these areas; (2) estimate the level of fluorine in the sediment/soil, and discuss its relationship with high fluorine level in the groundwater; and (3) evaluate the fluorine leachability in the aquifer and discuss the possible dynamics.

Sampling and analysis

Site description

Laizhou Bay is located in the northern part of Shandong Province, China, which is adjacent to Bohai Sea and Yellow Sea (Fig. 1). Its basement is a metamorphic sequence formed during the Archaean–Proterozoic Period. The sedimentary cover consists mainly of the Early Cretaceous Qingshan Formation, the Eocene Huangxian Formation, basalt and the Quaternary. The former is scarcely exposed and sporadically distributed around the border of this area. From Hutouya, through Changyi and Shouguang Counties, to the west of Xiaoqing River, the Quaternary comprises the Upper Pleistocene and Holocene Periods. The Upper Pleistocene layer, which consists of alluvial or diluvial, mild clay, sandy clay, fine to coarse sands and gravels, usually 10–100 m in thickness, is the main aquifer in the study area. Three brine/salt aquifers occur, respectively, in the Holocene, Upper Pleistocene and Lower Pleistocene (Xue et al. 1998).

Two cores were extracted in 2009 in the northern part of Tushan Town, Laizhou City and Puzhuang Town, Changyi City. The two towns have severely high fluorine contamination in the groundwater (Han 1997; Chen et al. 2011). There were an estimated 93,388 cases of dental or skeletal fluorosis in Changyi City and 15,600 cases of dental or skeletal fluorosis in Laizhou City in 2001. In addition, the region suffers from seawater intrusion as a result of its close proximity to the Bohai Sea, including modern seawater and the brine/salt (paleo-seawater) intrusion (Meng et al. 2002).

Sampling and analysis methods

The sedimentary cores were obtained with a piston corer. The locations of the cores are shown in Fig. 1. The core from Tushan Town (TS) was extracted from the northern part of Laizhou City, with the geographical coordinate of N37°06.5460′, E119°40.1753′. The core from Puzhuang (PZ) was situated at N37°03′17.3″ E119°32′13.9″. The length of TS sediment core is 40 m, and the PZ core is 80 m. Both of the core samples represent a cross-section of the four, main aquifers.

The cores were cut into sections according to the description of lithology. Then, the sections were sealed in plastic tapes and expeditiously sent to a laboratory. Half of the sediments were frozen until further analysis could be performed. The remainder was dried at room temperature, ground using an agate mortar and pestle; and a fraction was passed through a 2 mm sieve, and then it was collected for analysis. The method to determine the fluorine content was designed by McQuaker and Gurney (1977) utilizing a fluoride selective electrode (DZ/T0167-2006). The accuracy of analysis was checked by comparing the samples with the standard, controlled samples, and the errors for all analyzed samples proved to be less than 5 %.

Simulation experiment methodology of fluorine leaching ability

To directly reveal the dynamics of groundwater fluorine enrichment in coastal areas, a fluorine leaching experiment of rocks was conducted in laboratory. The starting

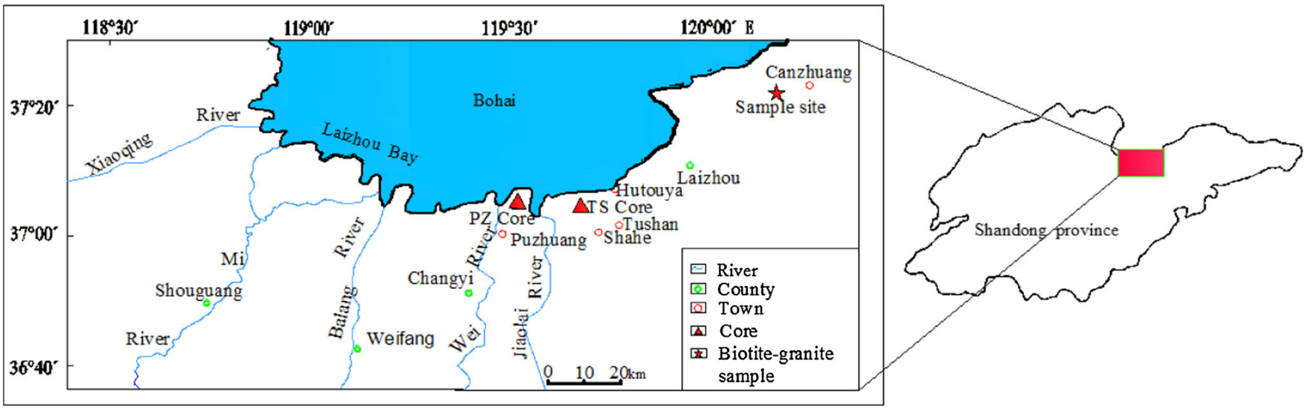

Fig. 1 Geographical map of Laizhou Bay and the sampling sites

materials were fresh water, seawater, brine water, and the biotite granites.

Two types of seawater intrusion are involved along Laizhou Bay: modern seawater intrusion and brine/saline water intrusion derived from paleo-seawater in shallow Quaternary sediments (Meng et al. 2002; Chen et al. 2012). Hence, the fresh water, fresh water and seawater of 1:1, and seawater were used to determine the difference of fluorine leachability with the addition of seawater. The fresh water, fresh water and brine water of 1:1, and brine water were used to reveal the difference of fluorine leachability with the addition of brine water. Totally, five solutions were prepared.

Fluorine enriches in late-stage pegmatite granites because it is an incompatible element, and fluorine is associated with biotite due to its similar radius to OH^-. Therefore, the biotite granites have high fluorine levels and are used as experiment samples in this study. The rock samples were collected from Moshan magmatic body in Canzhuang Town, Yantai City, Shandong Province, a representative outcrop of biotite granite (Fig. 1). The magmatic body lies in the northeast of the sediment cores and belongs to Linglong-type granite. The rocks are approximately composed of 40 % κ-feldspar, 30 % plagioclase, 25–26 % quartz and 3–5 % biotite; and some accessory minerals as magnetite, garnet, and allanite were detected in small concentrations (Luo and Miao 2002).

The rock samples were crushed into particles less than 100 mesh. Five 1,000 ml beakers were pre-cleaned and 50 g of the sample was added into each beaker. Then, the beakers were immersed, respectively, with 1,000 ml of the prepared five solutions and placed on bench; 120 ml supernatant were withdrawn from each beaker with a syringe on various occasions (8, 16, 24, 48, 96 and 192 h). Every beaker was shaken by magnetic stirrer for 1 min to facilitate mixing after each sampling (Fig. 2). The fluorine levels of the solutions were determined using fluorine selective electrode.

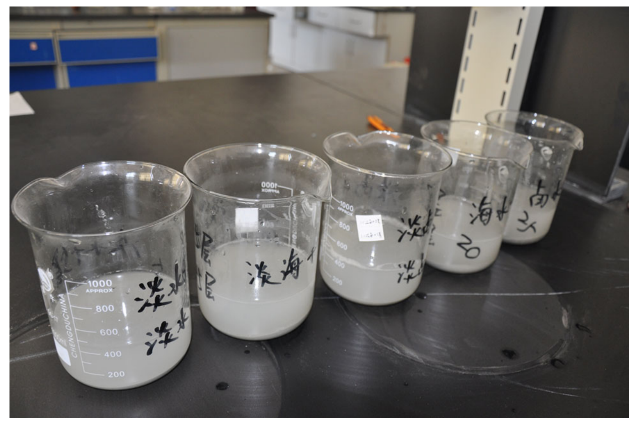

Fig. 2 The simulation experiment in laboratory

Results and discussions

Sediment characteristics of the aquifer

The sedimentary structure, colors and classified sedimentary facies were described on each section of the two cores as shown in Fig. 3. The two cores are mainly composed of clay, silt clay, and small amounts of coarse sand with granule gravels. Four aquifers were found at 25.9–34.7, 46.9–51, 60.5–62, 71.9–79.3 m in the PZ core and 13.5–15.7, 17.8–18.9, 25.1–27.0, 30.2–36.5 m in the TS core. In addition, two calcareous nodule layers were observed at a depth of 41–41.5 and 56.95–57.1 m in the PZ core.

The sediments of the four aquifers were photographed in Figs. 4 and 5. Both cores revealed that the aquifers are mainly composed of granite gravels. Fluorine is classified as an incompatible, lithophile element (Faure 1991), which means that it preferentially partitions into melts as magmatic crystallization proceeds (Xiong and Zhu 1998). As a result, hydrothermal vein deposits, late-stage pegmatite granites and rocks that crystallize from highly evolved

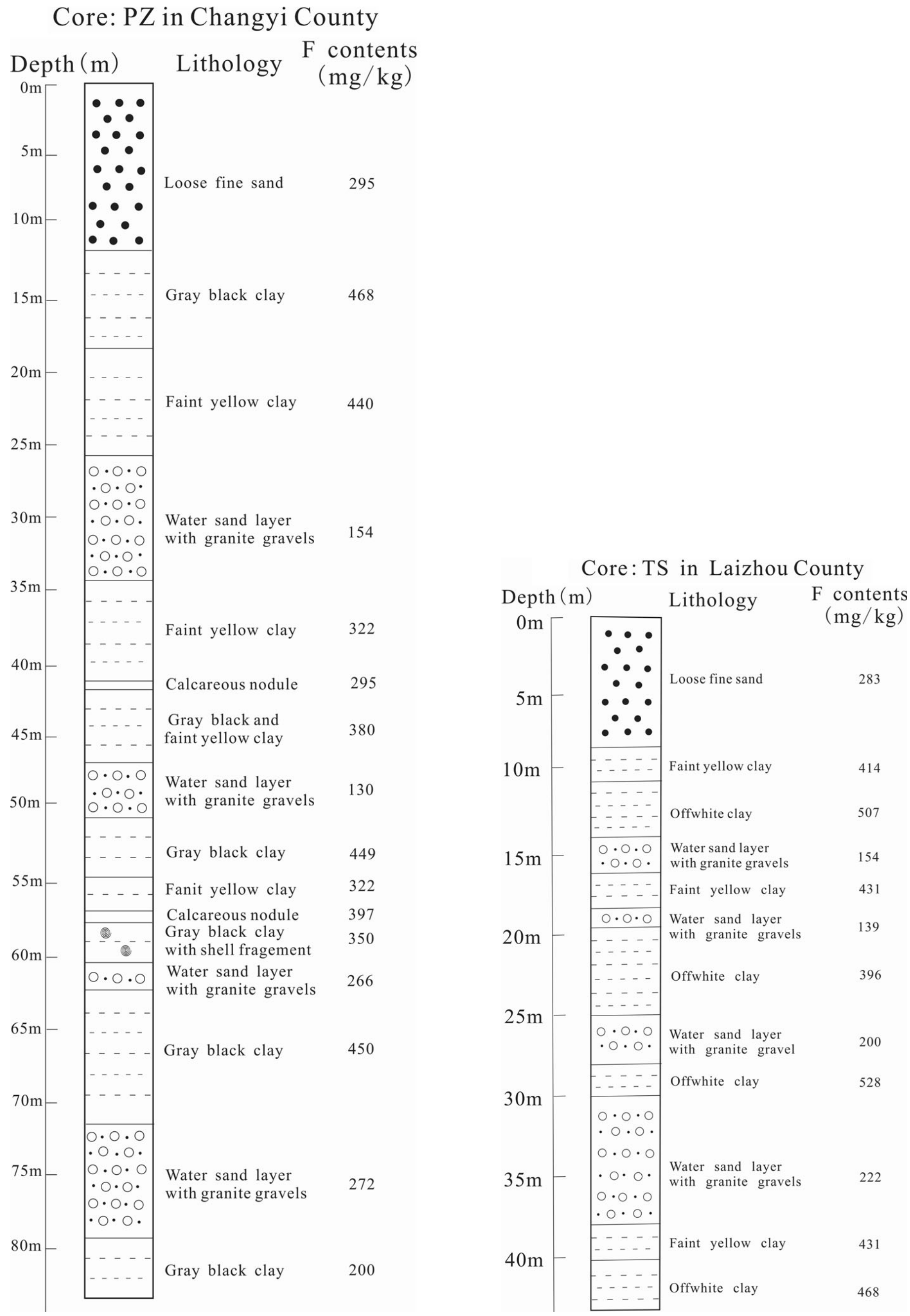

Fig. 3 The lithology and fluorine contents of the two sediment cores

magmas often contain fluorapatite, fluorite and fluoride-enriched micas and/or amphiboles (Nagadu et al. 2003; Taylor and Fallick 1997; Scaillet and Macdonald 2004).

Fluorite is considered as the dominant source of fluoride in groundwater, especially in granitic terrains (Kim and Jeong 2005). However, its solubility and dissolution rate is slow (Kim and Jeong 2005). Therefore, some researchers suggest that minerals influencing the hydrogeochemistry of fluoride include apatite, cryolite, villiaumite and silicates such as the double-chain silicates of amphiboles, the phyllosilicates of micas, and the phyllosilicates of clays where F^- and OH^- substitutes for each other within their octahedral sheet (e.g., Chae et al. 2006; Subba Rao and John Devadas 2003). Therefore, the minerals of the granite gravels in this area seem to provide fluorine ions. In fact, a number of researches argued that fluorine leaching into the groundwater is associated with granite and gneiss. Chae et al. (2007) confirmed that the high levels of fluoride in the groundwater in South Korea have been identified in the sedimentary aquifers that are made up of fluoride-bearing minerals derived from parent rocks of granites. Fantong et al. (2010) reported that the occurrence of toxic

Fig. 4 The sediments in the aquifers of the TS cores (the pictures on the lower right present the wet sediment)

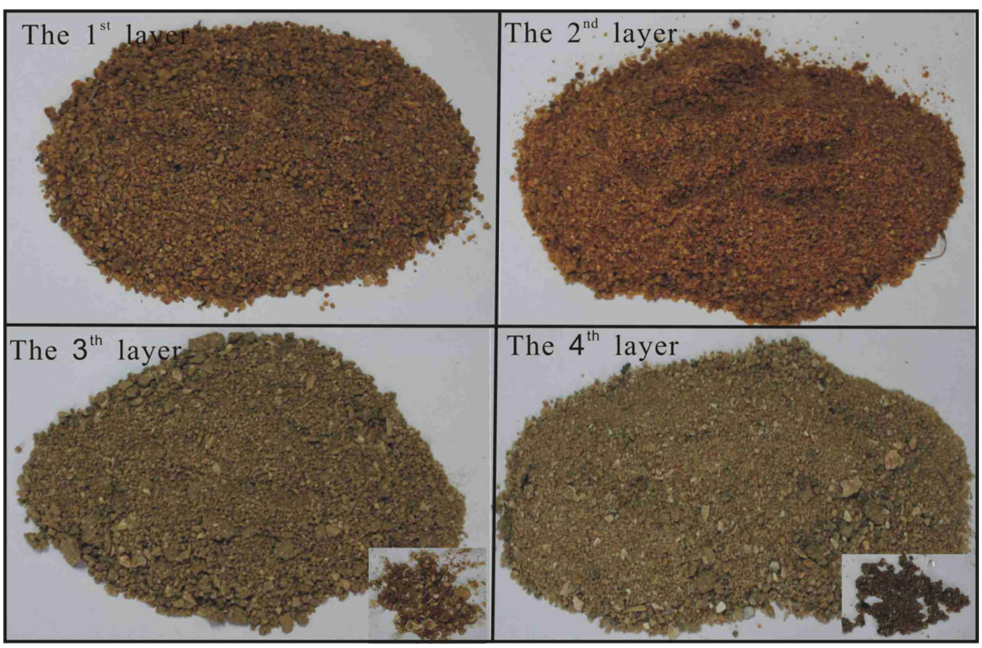

Fig. 5 The sediments in the aquifers of the PZ cores (the pictures on the lower right present the wet sediment)

concentrations of fluoride in groundwater in Mayo Tsanaga River Basin, Cameroon is linked to dissolution of fluoride-rich minerals in the granites. Valenzuela-vasquez et al. (2006) stated that the fluoride in the groundwater supply to Hermosillo City, Sonora, Mexico originates from granites from the Sierra Bachoco basement. In other places such as Kitakami Mountains, Northeast Japan (Kanisiwa 1979), Sor Rondane Mountains, East Antarctica (Li et al. 2003), Nalgonda District, India (Reddy et al. 2010), granites are proved to provide abundant concentrations of fluoride in groundwater. The authors' observations are in agreement with these results.

Granites occur widely, surrounding the coastal region of Laizhou Bay, especially in the northwest part (Fig. 6). Luo and Miao (2002) classified the granites into Aishan-type, Guojialing-type, Luanjiahe-type and Linglong-type and

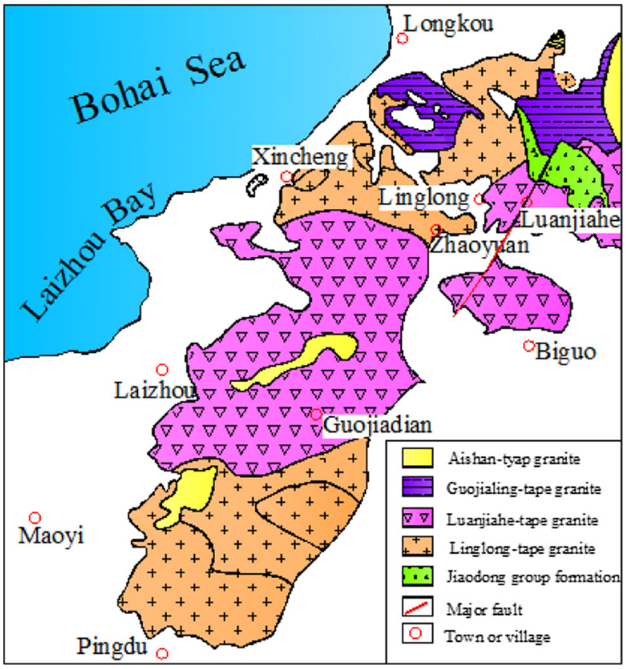

Fig. 6 Granites surrounding Laizhou Bay (after Luo and Miao 2002)

concluded that the granites were formed during late Yanshanian Phase of Mesozoic Period.

There are few reports detailing the sources and enrichment dynamics of groundwater with high levels of fluorine in Laizhou Bay. Li (2007) reported that the surrounding Cretaceous clastic, lava rocks of the Qingshan Group and sedimentary clastic rocks of the Wangshi Group are the sources of fluorine, due to the relative high contents and leaching coefficients of fluorine. But the data show its levels of fluorine vary from 440 to 600 mg/kg, which are equal to or even lower than the national average of 625 mg/kg in rock (Xie et al. 1999). The authors' investigation suggests that the source of fluorine should be focused around the granites of the Yanshanian Phase in the coastal area of Laizhou Bay.

Fluorine contents of sedimentary cores

The levels of fluorine in the sediment of the four aquifers are listed in Fig. 3. The fluorine level of the TS core ranges between 139 and 528 mg/kg, with an average of 348 mg/kg. The PZ core has fluorine levels as high as 130–468 mg/kg and a mean of 324 mg/kg. The national average of fluorine in the soil or sediment is 453 mg/kg. Wang and Wei (1995) summarized soil samples developed from different rocks in China and proposed that the average value is much higher. Therefore, the cores in this area show a relatively lower level of fluorine, and fluorine enrichment in the groundwater should not be attributed to the sediment itself in this area. The levels of fluorine in the TS core are in this order: off-white clay > faint yellow clay > loose fine sand > sands layer. The fluorine levels for PZ core layers are as follows: gray black clay > faint yellow clay > calcareous nodule > loose fine sand > sands layer. The similar orders of the two cores may be attributed to the same deposition environments.

The sediments in the aquifer show the lowest levels of fluorine. The average fluorine concentrations from top to bottom are 154, 139, 200, 222 mg/kg for the TS core, and 154, 130, 266, 272 mg/kg for the PZ core, respectively. Such low levels of fluorine in the granite gravels in the two cores indicate that a vast amount of fluorine was released into the groundwater during the interaction between the rock and water. Although there is still no document that dates the level of fluorine in granite gravels in aquifers, it is acknowledged that the level of fluorine in the granites shows high concentrations. Vinogradov concluded that fluorine content in the granites had an average value of 660 ppm (Wang 1988), and even higher concentrations were reported. Rammohan Rao et al. (1993) reported that fluorine concentrations in granitic rocks from the Nalgonda District ranges from 325 to 3,200 mg/kg with a mean of 1,440 mg/kg. Fluorine in granites in the southwestern part of Japan reaches 810 ppm (Ye 1984). Li et al. (1985) showed fluorine in granites of Fang City, Henan Province, reached an average of 1,312 ppm. Zhu et al. (2002) compared fluorine concentrations of Li–F granitic rocks from different regions all over the world, which showed a range of 600–2,360 ppm with an average of 1,368 ppm. Brehler and Fuge (1974) summarized that most granites show a range of 200–2,000 ppm. Whereas, Wang (1988) stated that the level of fluorine in the granites in Zhaoyuan-Yexian (also namely Laizhou) area, a region surrounding Laizhou Bay, showed an average level of 590 ppm by a vast amount of samples, even slightly lower than the average. This implies that the level of fluorine in fresh granites around Laizhou Bay does not show high values.

The levels of fluorine in the sediment in the aquifer for the two cores both are characterized by the orders of 2nd, 1st, 3rd and 4th, indicating a similar sedimentary evolution. The fluorine which leached into the groundwater is associated with the resident time (Brunt et al. 2004; Saxena and Ahmed 2001). However, both cores show lower fluorine concentrations in the upper two layers of sediments than those of the bottom. This may be due to the fact that water in the upper two layers is heavily consumed by the local habitants, and as a result, the groundwater cycles more quickly, and fluorine leaching from granite gravels is intensified.

Simulation experiment of fluorine release with different solutions and the possible dynamics of fluorine enrichment

Although Wang (1988) stated fluorine concentration in granites around this area is almost equal to the average concentration, the granite gravels in the aquifer show extremely low values. It can be estimated that approximately 70 % fluorine in granite is leached into groundwater with the following equation if the fluorine concentration of 590 mg/kg (reported by Wang 1988), the average of the neighboring granites, is considered:

$$F_l\ (\%) = \frac{F_r - F_s}{F_r} \times 100\,\%$$

where F_l is the percentage of fluorine leachate, F_r is the fluorine contents in fresh granites, and F_s is the fluorine content in granite gravels.

Although the granites do not show higher levels of fluorine around Laizhou Bay, they show high leachability. Rocks determine the amount of fluorine in groundwater from two aspects: Fluorine in the rock itself (Subba Rao and John Devadas 2003) and conditions for leaching (Dowgiatto 2000; Woo et al. 2000; Smedley et al. 2002). Therefore, the release of fluorine is largely governed by the presence of other environmental conditions. One of the most distinctive geologic features in this area is seawater intrusion, which might alter groundwater properties and enhance fluorine leachability.

First, groundwater Na^+ increases when seawater is intruded, and Ca^{2+} decreases due to alkaline condition. Na^+ and Na^+/Ca^{2+}, therefore, increase owing to the seawater intrusion (Wu et al. 1994; Zhang and Peng 1998; Lamia et al. 2009). Such a process potentially promotes fluorine solubility because of the following two reasons: NaF has higher solubility than CaF_2 in water solution, and Na^+ has more of an affinity to F^- than Ca^{2+} or Mg^{2+}. Several experiments have confirmed that fluorine leachate increased with an increase of Na^+ and Na^+/Ca^{2+} (Krainov and Petrova 1976; Krainov and Zakutin 1994; Gao et al. 2007b). The inverse correlation between F^- and Ca^{2+} are often observed in the saturation state (Ozsvath 2009) because the maximum concentration of fluorine is generally restricted by CaF_2 (Apambire et al. 1997; Cronin et al. 2000; Saxena and Ahmed 2003).

Second, HCO_3^- in groundwater was considered as a fluorine enrichment factor due to the following reactions when Na^+ and HCO_3^- are adequate (Rammohan Rao et al. 1993; Saxena and Ahmed 2001, 2003; Subba Rao and John Devadas 2003):

$$CaF_2 + 2HCO_3^- = CaCO_3 + 2F^- + H_2O + CO_2 \quad (1)$$

$$CaF_2 + 2NaHCO_3 = CaCO_3 + 2Na^+ + 2F^- + H_2O + CO_2 \quad (2)$$

Obviously, more CaF_2 in rocks dissolved with an increase in $NaHCO_3$. Thereby, the increased HCO_3^- in groundwater due to seawater intrusion may be a main dynamic of the high fluorine leachability.

Third, seawater intrusion results in alkaline water. F^- and OH^- often replace each other within minerals because of the similar ionic radii. Especially in an environment with a high pH, OH^- often displaces F^-, and F^- is then released into the groundwater (Sreedevi et al. 2006). Therefore, groundwater with a high level of fluorine usually also has a high pH value. Alkaline water promotes the release of fluorine and many researches have observed that fluorine leaching is enhanced as the pH increases (Chae et al. 2007; Chen et al. 2012).

In addition, many studies demonstrated that fluorine enrichment is favored by high salinity, conductivity, TDS and hardness (Ahmed et al. 2002; Chae et al. 2006; Valenzuela-Vasquez et al. 2006; Gao et al. 2007b; Jiang 2008). Such conditions obviously occur due to seawater intrusion and consequently fluorine leaching from rock increases.

A series of studies on fluorine sources and the forming factors in aquifers also concluded that there is a close relationship between high concentrations of fluorine and soft, alkaline groundwater that has low concentrations of Ca^{2+} and high concentrations of Na^+ (Robertson 1986; Whittemore et al. 1993; Kierdorf and Kierdorf 2000; Woo et al. 2000; Earle and Krogh 2004; Nordstrom and Ball 2005; Chae et al. 2006, 2007; Walna et al. 2007). In fact, investigation also found that the distribution of fluorosis and the patterns of seawater intrusion in Laizhou Bay have the same trends (Chen et al. 2011, 2012).

More interesting, the simulated results of fluorine leaching from biotite granites are shown in Fig. 7. Figure 7a indicates fluorine leachability with the addition of seawater. The increased fluorine ions for fresh water solution increase before 24 h, and reach the minimum value of 0.04 mg/L at 48 h and the maximum value of 1.12 mg/L at 96 h, and then begin to decrease at 192 h. The increased fluorine for fresh water and seawater of 1:1, and seawater solutions both have the minimum values of 0.28 and 0.32 mg/L, respectively, at 16 h, and besides that for fresh water and seawater of 1:1 solution shows a decreasing trend after 48 h. Figure 7b describes the fluorine concentrations with different mixing of brine water. The fluorine concentrations for the fresh water and brine water of 1:1 solution increase before 24 h and decrease after 96 h, with a maximum of 8.38 mg/L at 48 h. The brine water shows fluorine trend of decreasing from 8 h to 16 h and increasing after 24 h, with the minimum of 4.58 mg/L at 16 h. Generally, the leaching fluorine for five

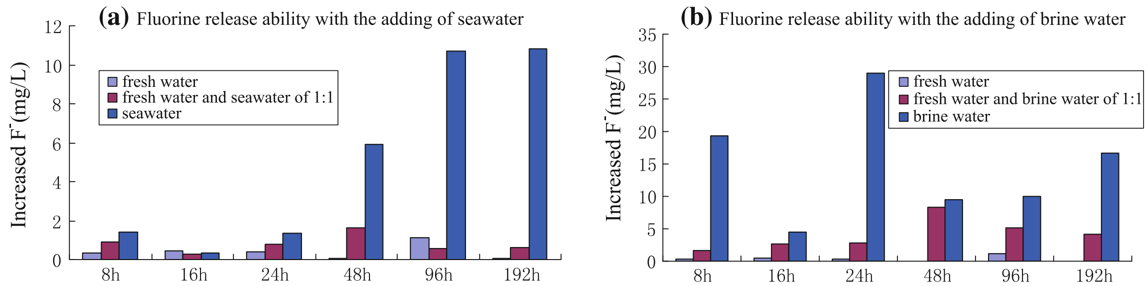

Fig. 7 Simulated results of fluorine release from granites with different solutions

solutions seems to show different variations. One reason may be the complex water–rock interactions process as transformation, self-purification, absorption, dissolution and sedimentation and so on. The other reason is probably attributed to the strong ion exchange interaction during the mixing of seawater and brine water, which influences fluorine levels by changing the equilibrium of Na–Ca–F (Xue et al. 1998; Meng et al. 2002). Also, Wang et al. (2008) found the similar process of Ca^{2+}, SO_4^{2-}, Cl^- during water–rock interaction.

Despite the complexity of fluorine leaching from rocks, it can be found that the increased fluorine is in the order: seawater > fresh water and brine water of 1:1 > fresh water, and brine water > fresh water and brine water of 1:1 > fresh water, except a slightly higher value for fresh water at 16 h and a slightly lower value for the fresh water and brine water of 1:1 at 96 h. Obviously, the fluorine release ability increases with the adding of seawater or brine water, and such a fact directly confirms that the leaching ability of soil/rock is enhanced with seawater or brine water intrusion in coastal areas.

In fact, not only in the coastal area along Laizhou Bay, but also in other regions, high fluorine concentrations in groundwater occurred in seawater intrusion areas. For example, a high incidence of fluorosis along the coastal region of Liaoning Province, China was found (Kou and Wang 2000). Further, salt lake water intrusions, a process similar to seawater intrusion, take place in Yuncheng, Shanxi Province of China and Nagar Parker, Sindh Province of Pakistan, and experiments have confirmed to increase rock fluorine leachability and elevate fluorine concentrations due to the under saturation with respect to fluorite in these areas (Gao et al. 2007b; Tahir et al. 2009).

Conclusions

Two sediment cores were drilled in Changyi County and Laizhou County along Laizhou Bay, where the widespread fluorosis of drinking water occurs. The fluorine concentrations in the two cores were studied to determine the sources of fluorine in the groundwater and the enrichment dynamics, and the following was ascertained:

1. It was found that the sediment in the aquifer was composed of weathered, granite gravels. Thus, the granites of the Yanshanian Phase, widely distributed in the northeastern part of the coastal region of Laizhou Bay, seem to be responsible for the enrichment of groundwater with fluorine. Such a result is in agreement with the previous findings.
2. The fluorine concentrations of the PZ and TS cores range at 130–468, 139–528 mg/kg, with average values of 324, 348 mg/kg, respectively. They do not show high levels, the levels of fluorine in sediment cannot explain the fluorine enrichment in groundwater. However, the average fluorine concentrations in the aquifer from top to bottom are 154, 139, 200, 222 mg/kg for the TS core, and 154, 130, 266, 272 mg/kg for the PZ core, respectively. This shows extremely low levels of fluorine and indicates that a vast amount of fluorine was leached into the groundwater.
3. The document showed fluorine concentrations in the granite surrounding Laizhou Bay are almost equal to or even lower than the average values; however, the leachability of fluorine is approximately 70 %. One of the most distinctive geologic features in this area, the existence of seawater intrusion, may potentially enhance the ability of fluorine to leach into the groundwater. Meanwhile, the simulation experiment also indicates that fluorine leaching from rocks increases with the adding of seawater or brine water.

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