HYDROGEOCHEMISTRY OF FLUORINE IN GROUNDWATERS OF ISPARTA, SW TURKEY

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ABSTRACT

The Gölcük area represents a post-tectonic Pliocene volcanic field upon a Mesozoic paleorift in the Western Taurides, Turkey and consists of sedimentary and volcanic rocks. The volcanic rocks of an Na and K-alkaline sequence are pyroclastic tuffs (stage i), tephriphonolites (stage ii) and trachyandesites and trachytes with pyroclastic tuffs (stage iii). The volcanic rocks consist primarily of pyroxenes, hornblendes, sphenes, biotites, fluorites, fluorapatites, and glassy groundmass as potential fluorine carriers, This florine-bearing groundmass is an essential reason for the high fluorine contents of the drinking waters of the province capital Isparta with about 200.000 inhabitants. In shallow aqueous systems within the volcanic rocks of the Gölcük area in Isparta and environs, high fluorine contents up to 6.0 mg/l were measured which are higher than those of sedimentary rocks. Fluorine ions are leached mainly from glassy groundmass of the Na and K-alkaline volcanic rocks, lesser from fluorine carriers such as pyroxenes, hornblendes, biotites, phlogopites and fluorapatites. Fluorine contents in groundwaters within these volcanic rocks of Gölcük area are limited by the solubility of fluorite, i. e. also by Ca^{2+} values. Due to low pCO_2 in the barren soils of pyroclastic tuffs such as friable tuffs, pumice tuffs and ignimbrites , calcite dissolution is limited. Low Ca^{2+} concentrations are enhanced by Na^+ versus Ca^{2+} ion exchanges. Moreover, F^- versus OH^- ion exchange is at high pH values due to calcite dissolution with low pCO_2. Finally, it can be deduced, that not only one single reason is the cause for the high fluorine contents measured in shallow aqueous systems, but also a concurrence of several natural factors.

1. INTRODUCTION

High fluorine contents in drinkin waters are not only interesting from the geochemical point of view, but also cause dental and medical problems. Fluorine is also an essential trace element for human healt, but excessive intake may lead to problems for bones and teeth. The deficiency of fluorine in drinking waters causes a caries efffect of the teeth, while high contents generate fluorosis (Fig. 1; Bhussry et al., 1970; Jenkins et al., 1970; Matousek and Hoehn, 1986; Zhaoli et al., 1989). Therefore, the highest permissible value in drinking waters is limited, depending upon annual average temperatures, by the WHO and many other national standards to 1.0-1,5 mg/l. Generally, the fluorine contents in aqueous dystems lie between 0,05 and 0.5 mg/l (Quentin, 1957), i.e. normally fluorıne contents in aqueous systems are so low, that supplementary fluorine must be added, especially for children.

In comparison to other halogenes, fluorine in aqueous systems is not mobile and usually limited in aqueous solutins, mainly by the mineral phase fluorite (CaF_2), respectively by Ca^{2+} contents. In some cases fluorine is controlled by the relatively low soluble mineral phase fluorapatite [$Ca_5(F,OH)$ $(PO_4)_3$]. As an ubiquitous element Ca^{2+} encountered as one of the main dissolved constituents in most aqueous systems. The solubility calculations using PHREEQE (Parkhurst et al., 1980) show that, under equilibrium conditions, the Ca^{2+} contents should not exceed 100-200 mg/l to keep the highest permissible value of 1.0-1,5 mg/l fluorine in solutions. Such Ca^{2+} contents are world-wide commen for most of the aqueous systems. Theoretically, it is the quantity of calcite dissolved in an open system to pCO_2 of about 0.03 (3 percent of total atmosphere pressure; Pekdeğer et al., 1992). Such pCO_2 values are encountered generally in gas of fertile soils.

2. GEOLOGIC SETTING

The Gölcük area is located in SW of Isparta and represents the post tectonic Neogene volcanism upon a Mesozoic Paleorift of the Western Taurides (Poisson et al., 1984), the so called Isparta angle between Lycian and Hadım-Hoyran-Beyşehir nappes (Fig. 2). As allochthonous, the Triassic through Upper Cretaceous Akdağ limestone and the Upper Cretaceous to Lower Tertiary volcano-sedimentary series constitute the basement rocks (Özgür et al., 1990; Özgür et al., 2008; Elitok et al., 2010). The both basement rocks are transgressively overlain by marine clastic series of Eocene and conglomerates of Oligocene age. The volcanic sequence is of a Na and K-alkaline character, has an age ranging from Lower Pliocene (5.77 ± 0.22 Ma: Kamacı et al., 2009) to Pleistocene (24.000 ± 2.000 a; Özgür et al., 2008; Elitok et al., 2010) and include pyroclastic series of trachyandesitic and trachytic character, tephriphonolites and trachyandesitic and trachytic lava flows. The development of the volcanism can be temporally divided into three stages (Özgür et al., 2008; Elitok et al., 2010; Fig. 3) : (1) pyroclastic series, (2) tephriphonolites and (3) pyroclastic series with trachyanesites and trachytes as dikes, vents and domes. The pyroclastic series consists of friable tuff (150-200 m), ignimbrite (20 m) and pumice tuff (10 m) dominating landscape. Generally, the volcanic rocks consist primarily of varying constituents of K (Na)-sanidine, oligoclase, biotite, pyroxene, hornblende, pyroxenitic xenolithes, glassy groundmass and minor quantities of apatite, fluorite and sphene c ommon. Moreover, tephriphonolites contain augite and nepheline additionally.

Fig. 1. Brittle and weared teeth of an ihhabitant in Isparta due
To intake of higher doses of fluorine for a longer time.

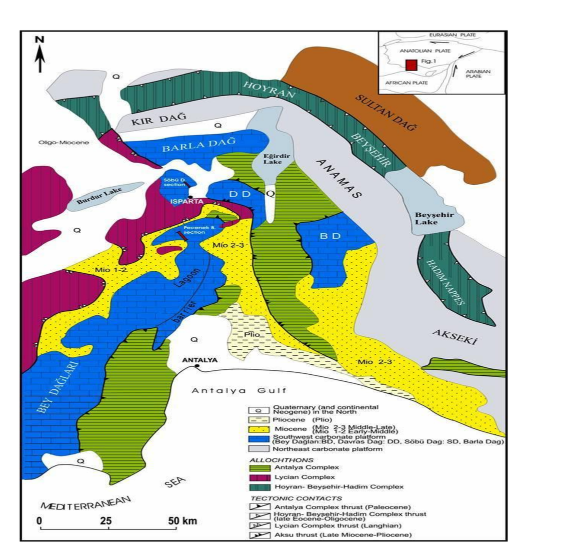

Fig. 2. Location map of the study area and Geotectonic position of the Isparta angle.

3. GEOCHEMISTRY

During the geological mapping of the Gölcük area 220 rock samples have been collected (Pekdeğer et al., 1992). Optical and geochemical analyses confirmed of the petrographic character of the various lavas according to which they can be divided into tephriphonolite, trachyandesite and trachyte (Fig. 4). Furthermore, the pyroclastic series indicate a composition between trachyandesite and trachyte. The volcanic rocks have high fluorine contents in a range from 33 to ppm and a background value of 1.000 ppm (Fig. 5) which can be attributed to different fluorine-bearing mineral phases. In general, there is a close correlation between fluorine and P_2O_5 (Fig. 6).

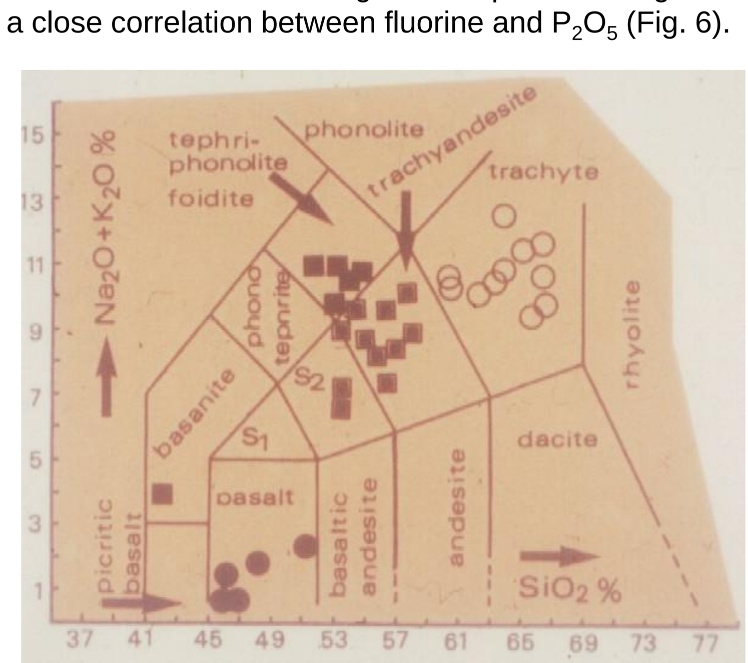

Fig. 4. Classification of volcanic lava flows and pyroclastic series (S1: Trachybasalt; S2: Shoshonite)

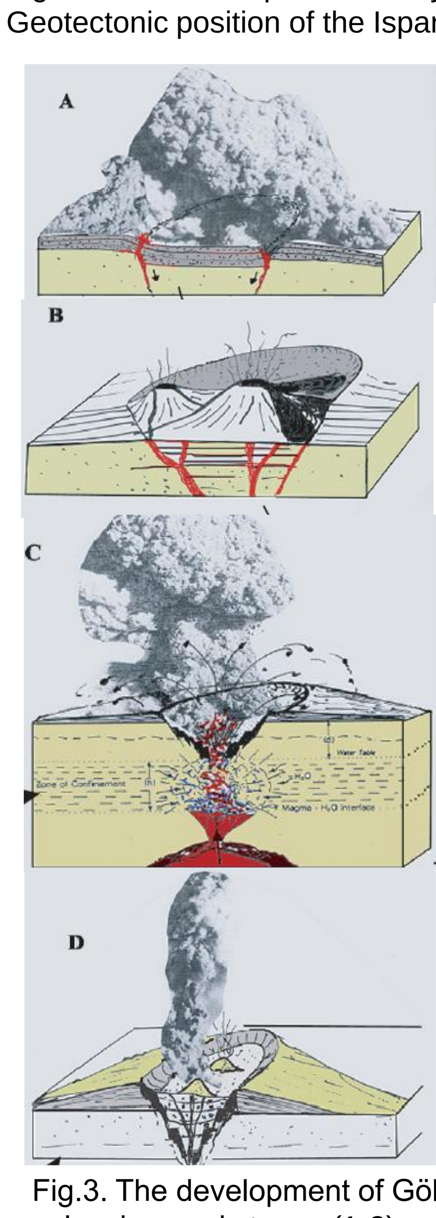

Fig.3. The development of Gölcük volcanism and stages (1-3).

4. HYDROGEOLOGY AND HYDROGEOCHEMISTRY

A small part of the drinking waters of the province capital Isparta comes from the Gölcük lake drainage area near Isparta. The Gölcük lake as a crater lake is mainly a build up of Pliocene volcanic rocks. Around the drainage area of the Gölcük lake semi-arid climatic conditions are present. The average annual rainfall 70 years is about 600 mm/a and the average annual temperature is 12 °C. The precipitation in this continental climate is principally in the winter months. The drainage area around the crater lake displays a funnel shaped geometry. The lake is supplied by rainwater and perennial springs and brooks. The underlying akdağ limestone and pyroclastic series are good aquifers. Volcanic rock series with differnt permeabilities form a number of aquifers and aquitards lying one above other. These both aquifers and aquitards are tilted towards the lake which is the main drainage area for the surface waters and groundwaters. In the field, the substantial amounts of groundwaters are infiltrating to the lake from the subsurface.

Fluorine contents in the groundwaters within the volcanic rocks of the Gölcük area range from 0,7 to 5,6 mg/l with an average of 2,5 mg/l (Fig. 7.). The groundwater in the sedimentary rock aquifers contains lesser than 0,7 mg/l (Pekdeğer et al., 1990; Pekdeğer et al., 1992) which also holds true for leachates from 40 leaching experiments carried out under controlled laboratory conditions with different rock types yielding fluorine contents between 0,2 and 6,6 mg/l (Pekdeğer et al., 1992).

5. HYDROGEOCHEMISTRY OF FLUORINE

To determine the reason for the high fluorine contents in the aqueous systems of the Gölcük area, there are three aspects to consider: (1) high fluorine in source rocks, (2) hydrothermal activity and fluorite stability. Moreover, the following aspects are of importance for determination the origin of fluorine in the aqueous systems:

(1)The volcanic rocks of the Gölcük area show fluorine contents in a range from 33 to 3200 ppm and a background value of 1.000 ppm which are related to differnt fluorine-bearing mineral phases (Fig. 5). There is a close correlation between fluorine and P_2O_5 in the volcanic rocks indicating geochemical role of fluorapatite as one of the important fluorine carriers. In comparison, the sedimentary rocks contain low fluorine contents in a range from 100 to 200 ppm

(2) There is an obvious differnce in fluorine contents in aqueous systems from the sedimentary rock series and the volcanic rocks. Fluorapatite and other well crystallized mineral phases such as biotite, hornblende, etc. are less important fluorine sources for these semi-arid hydrological and climatological conditions, also shown by a lack of alteration when examined microscopically.

(3) There is no recent activity around Gölcük lake. Out of the drainage area gas and hydrothermal outlets could be observed. There, water samples contain fluorine contents lesser than 1.0 mg/l. Furthermore, field observations show that even perennial springs within pyroclastic rocks in high altitude recharge areas exhibit higher fluorine contents than the mentioned hydrothermal waters. A quantitative contribution of hydrothermal activity to the high fluorine contents can, therefore, be ruled out.

(4) High fluorine contents in the groundwaters within the drainage area of the Gölcük lake correspond with low Ca2+ contents lesser than 40 mg/l. The lake water is mixed water with propositional chemical composition. The contents of Ca^{2+} and F^- are obviously limited by fluorite (CaF_2) solubility (Fig. 8). Fluorapatite which forms the other major fluorine-bearing mineral phase and may control the solution equilibria is highly supersaturated.

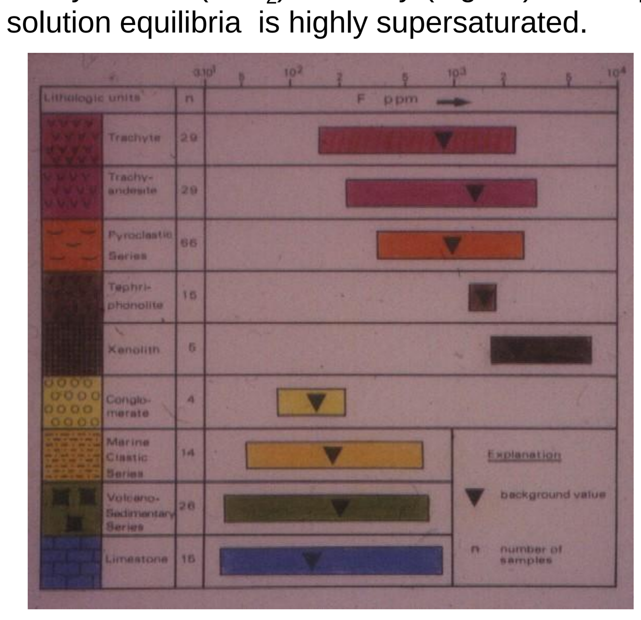

Fig. 5.Ranges and background values of fluorine in sedimentary and volcanic rocks of the Gölcük area.

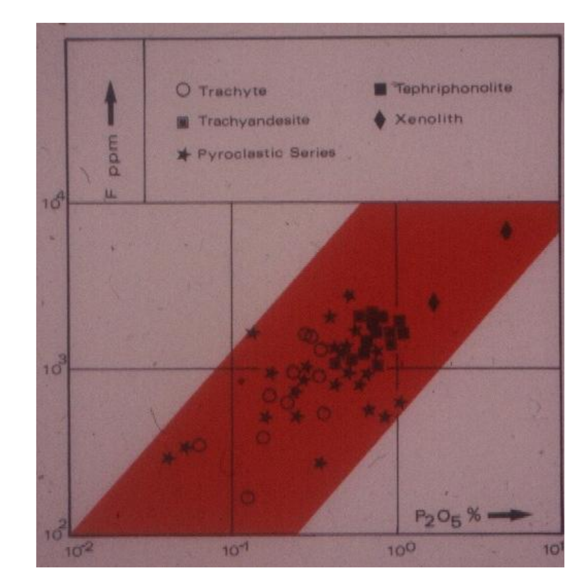

Fig. 6. A close correlation of F versus P_2O_5 in various volcanic rocks of the Gölcük area.

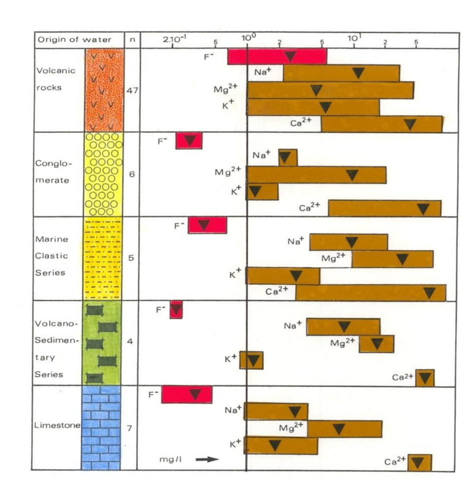

Fig. 7. Ranges and background values of fluorine in differnt waters of the Gölcük area.

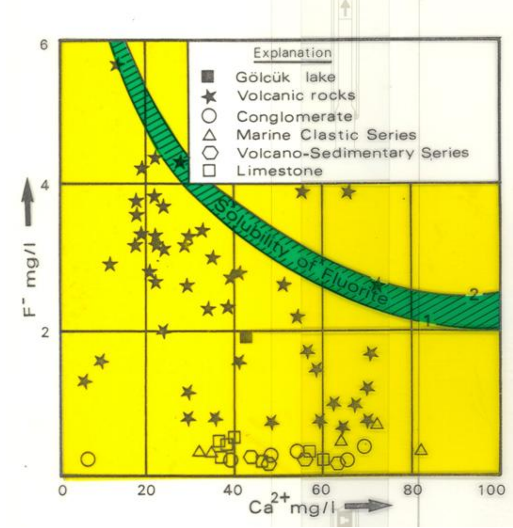

Fig. 8. F- and Ca2+ contents in the groundwaters within the volcanic rocks of the Gölcük area.

6. DISCUSSION

The low Ca^{2+} contents of the groundwaters are obviously not due to lack of calcite in the volcanic aquifers. Calcite is present in both volcanic and sedimentary rocks. Furthermore, the waters are saturated with respect to calcite. However, there is only a poor vegetation cover and little agricultural activity due to unfertile soils above the volcanic rocks and due to dry climatic conditions. This minimized microbiological activity leads to very low CO_2 contents (0,03-0,1 percent) in soil atmosphere as calculated from the carbonic acid system (Pekdeğer et al., 1992). The Ca^{2+} contents are accordingly low although in equilibrium with calcite (Fig. 9). Besides low Ca^{2+} contents, the resulting waters have high pH values due to low pCO_2 during calcite solution (Fig. 10). The pH values of the waters more than 8,0 also enhance exchange reactions between F^- and OH^- ions. Furthermore, the volcanic rocks of the Gölcük area are of Na and K-alkaline rocks, so that considerable amounts of Na^+ ions are dissolved during weathering. The Ca^{2+} ions are more readily adsorbed at the solid substance, in exchange adsorbed Na^+ ions go into solution. The groundwaters from the sedimentary rocks are of $Ca\text{-}HCO_3$ type, those from volcanic rocks $Na\text{-}Ca\text{-}HCO_3$ type.

Due to this ion exchange reaction, the Ca^{2+} contents decrease with increasing Na^+ contents. Contemporaneously, fluorine contents increase, so that there is a close correlation between Na^+ and F^- contents in aqueous systems.

Finally, it can be deduced, that not only one single reason is the cause for the high fluorine contents in the aqueous systems, but also a concurrence of several natural factors (Fig. 10).

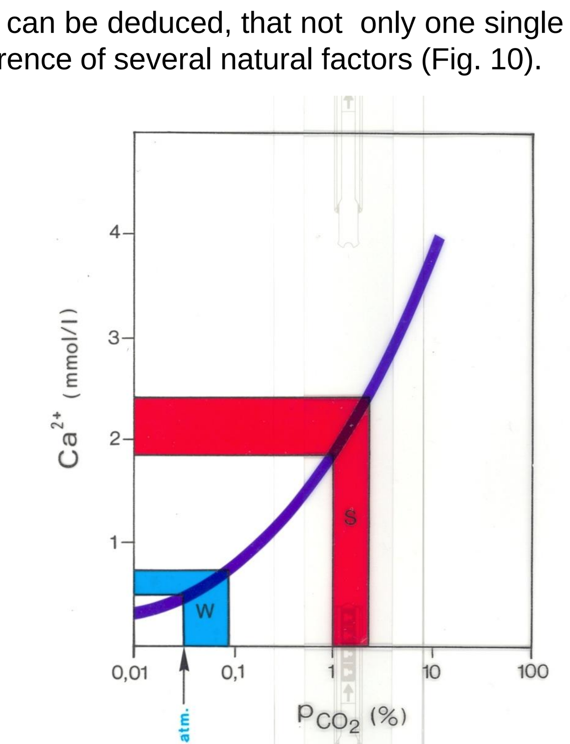

Fig. .9. Concent of Ca^{2+} in equilibrium with calcite as a function of pCO_2 (percent). Range of pCO_2 in groundwater (W) within the Gölcük area and in fertile soils (s)

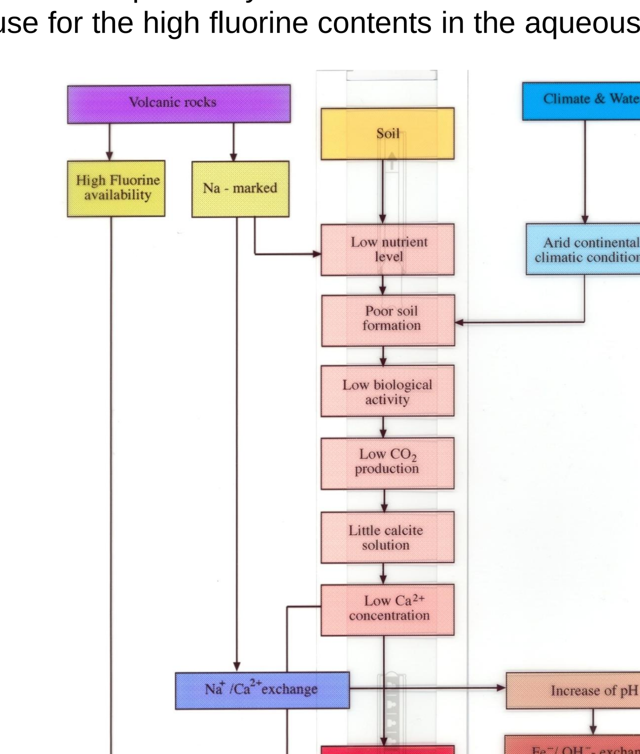

Fig. 10. Schematic flow of fluorine enrichment in the groundwaters of the Gölcük area.

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