

# The fluoride in the groundwater of Guarani Aquifer System: the origin associated with black shales of Paraná Basin

M. L. Kern · A. P. Vieiro · G. Machado

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**Abstract** This work presents petrological and geochemical results of the black shales interval from Permian and Devonian strata of the Paraná Basin, Brazil and its relationships with fluoride of groundwater from Guarani Aquifer System. The Guarani Aquifer, located in South Brazil, Uruguay, Paraguay and Argentine, presents contents of fluoride higher than the Brazilian accepted potability limits. Several hypotheses have been presented for the origin of the fluoride in the groundwater of the Guarani Aquifer. Microcrystalline fluorite was registered in black shales of Ponta Grossa and Irati formations from Paraná Basin. The results shown in this work suggest that fluoride present in groundwater of Guarani Aquifer can be originated in deeper groundwater that circulates in Ponta Grossa and Irati formations. The interaction of the groundwater coming from deeper black shales with the groundwater-bearing Aquifer Guarani System occurs through regional fragile structures (faults and fractures) that constitute excellent hydraulic connectors between the two sedimentary packages. The microcrystalline fluorite registered in Ponta Grossa and Irati Formations can be

dissolved promoting fluoride enrichment in groundwater of these black shales and Guarani Aquifer System.

**Keywords** Guarani Aquifer · Fluoride in groundwater · Hydrogeology

## Introduction

The Guarani Aquifer, located in South Brazil, Uruguay, Paraguay and Argentine, present contents of fluoride higher than the accepted potability limits in many wells. The fluoride ion ( $F^-$ ) is the most common form in which fluoride occurs in groundwater, although it may also be complexed with aluminum ( $AlF^{2+}$ ,  $AlF_2^+$ ,  $AlF_3$ ,  $AlF_4^-$ ), boron [ $BF(OH)_3^-$ ,  $BF_2(OH)_2^-$ ,  $BF_3(OH)^-$ ], calcium ( $CaF^+$ ), ferric iron ( $FeF^{2+}$ ,  $FeF_2^+$ ,  $FeF_3$ ) and magnesium ( $MgF$ ) as well as organic compounds (Nordstron and Jenny 1977). Aluminum ( $Al^{3+}$ ) and ferric ( $Fe^{3+}$ ) ions usually are not complexed with fluoride (because of their low solubility) in groundwater and tend to precipitate as gibbsite [ $Al(OH)_3$ ], goethite [ $FeO(OH)$ ] and in the presence of complexed iron, ferrihydrite ( $Fe_{10}O_{15} \cdot 9H_2O$ ). However, aluminum and ferric ions can play an important role in restricted, strongly acidic ( $pH < 4$ ) and oxidized ( $Eh > 0.0$  for  $Al^{3+}$ ;  $Eh > 0.8$  for  $Fe^{3+}$ ) environments (Brookins 1988). Magnesium ( $Mg^{2+}$ ) is an important agent for fluoride complexation in groundwater while calcium ( $Ca^{2+}$ ) is not relevant in this process because it forms mainly carbonates and sulfate complex ions. Calcium can also be combined with fluoride resulting in the calcium fluoride ionic species ( $CaF^+$ ), which is unstable in the groundwater (Gaciri and Davies 1993).

The origin of fluoride in groundwater can be related to both natural and anthropogenic sources. There are various minerals which have fluoride in this composition, but the

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source of this anion in groundwater is mainly related to the solubilization of fluorite (Stumm and Morgan 1981; Ashley and Burley 1995). The black shales of Ponta Grossa and Irati formations in the Paraná Basin contain microcrystalline fluorite. This black shale can be an important source of fluoride registered in the groundwater of the Guarani Aquifer System. It is important to mention that there are no published studies about the relationships between the origin of Guarani Aquifer groundwater fluoride and the black shales of Irati and Ponta Grossa formations.

The Guarani Aquifer System is constituted by the Botucatu Formation, which represents the main water-bearing unit; the Pirambóia Formation and Rosario do Sul Group (Araújo et al. 1995). More recent studies include the volcanic rocks of the Serra Geral Formation (Machado 2006). These lithostratigraphic units present a mineral composition incompatible with the high fluoride groundwater contents (up to 14 mg/l).

In acid waters ( $\text{pH} < 4$ ), fluoride occurs together with hydrogen ( $\text{HF}$  and  $\text{HF}_2^-$ ), which volatilizes at normal atmospheric pressure, and with silicon ( $\text{SiF}_6^{2-}$ ), which is stable at atmospheric pressure. The behavior of fluoride in groundwater is strongly dependent on pH and the solubility decrease in pH 6.0 up to pH 6.5. The increasing solubility of fluoride at acid pH values is due to formation of complexes with aluminum ( $\text{AlF}_2^+$ ,  $\text{AlF}_2^+$ ) and silicon ( $\text{SiF}_6^{2-}$ ), while higher pH values inhibit the adsorption of fluoride due to negatively charged clay minerals (Brookins 1988).

Hydrogeochemistry studies were carried out in some regions of the Guarani Aquifer (Fraga 1992; Kimmelman et al. 1989; Machado 2006; Marimon et al. 2007) showing a great compositional variation in this groundwater. The groundwater salinity and fluoride content are higher in the confined portions of the aquifer next to the central zone. Some hypotheses have been presented for the origin of the fluoride in groundwater of the Guarani Aquifer in the Rio Grande do Sul state. Lobo and Costa (1998) suggest a relationship of groundwater fluoride with a saline domo in the region of the Rio Pardo Valley, while Silvério da Silva et al. (2002) associate it with weathering of micas present in the crystalline basement and Triassic reptile fossils from Santa Maria Formation.

Hydrogeochemistry studies made by Licht et al. (1997) in the Paraná state correlate the high fluoride content of groundwater from Guarani Aquifer with intrusive subvolcanic alkaline rocks in the Paraná Basin.

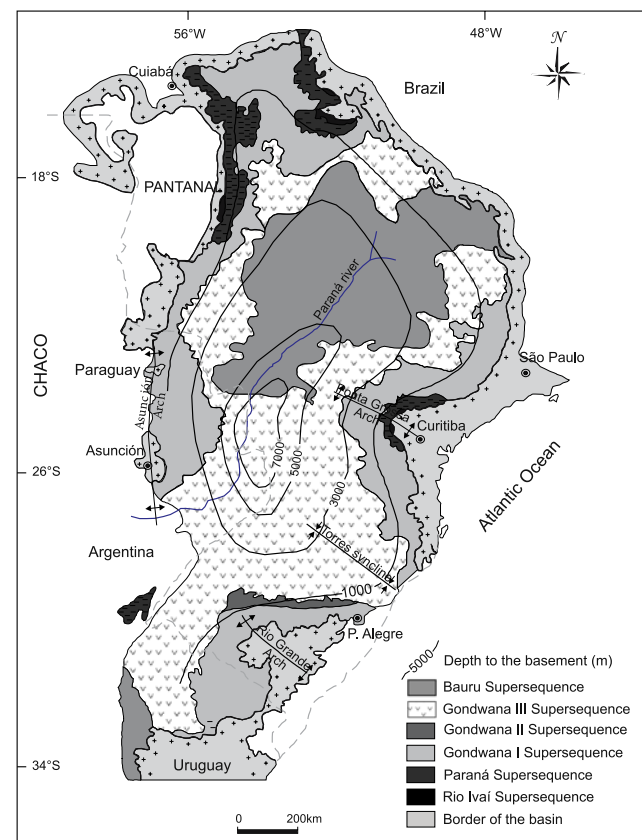
The Ponta Grossa and Irati Formations are composed mainly of mud rocks, such as lutites, mudstones, siltstones, limestones and black shales, (ca. 90% of total volume) that outcrop in Brazil extending for about 3,000 km from Aceguá in the southernmost part of Brazil to Jaciara and Cuiabá region in Mato Grosso state, in the West Centre-west region of the country (Figs. 1, 2). Besides the high

frequency of black shales in Paraná Basin, the total rock geochemical, petrography and mineral chemistry studies are reduced when compared with others sedimentary rocks from Paraná Basin. Probably, this is the principal reason for no establishments in specific literature of the relationship between fluoride in groundwater and black shales.

The current paper presents petrological and geochemical results on black shales interval characterization in Permian and Devonian strata from the Paraná Basin, Brazil, and their relationships with fluoride of groundwater from Guarani Aquifer. The relationship between groundwater fluoride origin and Irati and Ponta Grossa Formation have never been presented in previous studies.

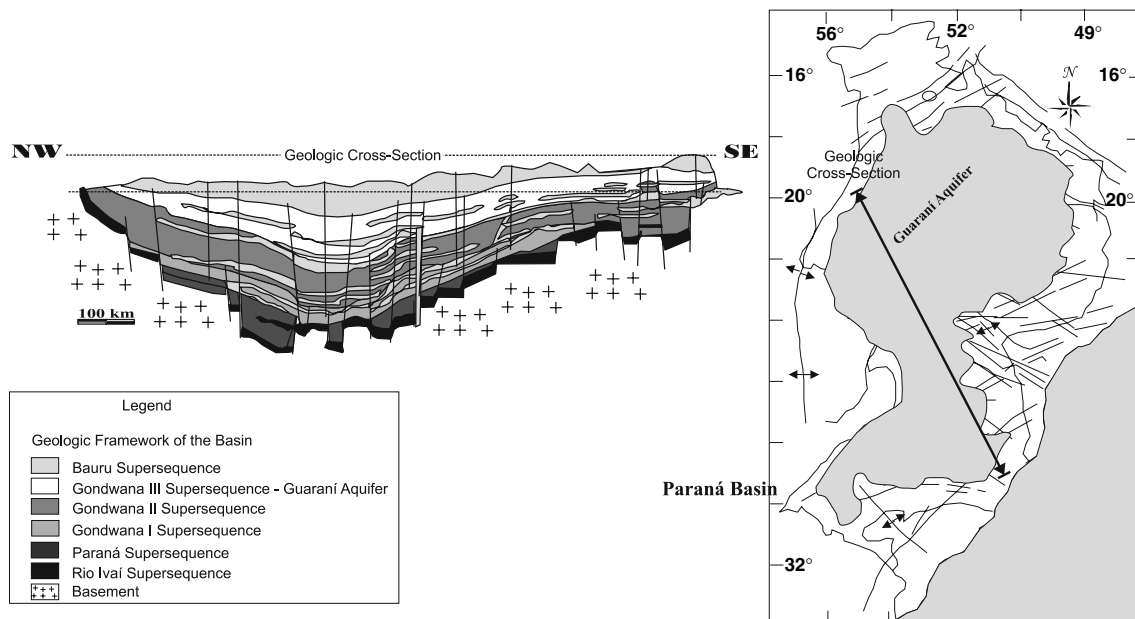
### Geological setting

The Paraná Basin is a vast sedimentary basin situated in central–eastern South America, including parts of Brazil, Argentina, Paraguay and Uruguay, with an area of about 1,500,000 km<sup>2</sup> (Fig. 1; Zalán et al. 1990). Eight Brazilian states are partially included in the area of the basin (Fig. 2).



**Fig. 1** Overview of the study area in the Paraná Basin of South America and the chronostratigraphic framework of the studied interval, modified from Zalán et al. (1990) and Milani (1998)





**Fig. 3** Geologic cross section showing the sequences and structural framework of the Paraná Basin (Assine 1996)

beds of either marine or terrestrial origin, making up the Itararé Group. This unit is composed by an association of sandstones, diamictites, conglomerates, and shales that reach 1.400 m of maximum thickness, (Milani and Zalán 1998).

The sedimentation included a large component of gravitational mechanisms, driven by the voluminous influx of clastics from those areas laid open by deglaciation. Rhythmic facies are common, as well as syndepositional deformation of strata due to slumpings. França and Potter (1988), using well log data, recognized three major fining-upward cycles in the glaciogenic package, probably reflecting climatic changes of higher order during the overall glacial time. Their cycles define a pattern of southward onlapping, related to a progressive expansion of the basin.

The Irati formation is a shaly section reaching a thickness of approximately 120 m, divided into three portions or members. The Irati formation represents a mixed dynamic system of siliciclastic and carbonatic sequences. The siliciclastic sequence predominates in the eastern portion of the basin and the carbonatic sequence prevails in the northern portion of the Paraná Basin (Araújo 2001).

Tectonically, the Paraná Basin forms a NE–SW ramp (Fig. 3), with a smooth inclination of about  $0.0015^\circ$  towards the southeast in its southern portion. Under this paleographic configuration, inherited because of the installation of a magmatic arc in the Permian, three different lithofacies associations were formed, which developed under depositional domains related to the carbonatic internal, intermediate and distal slope (Araújo 2001).

In terms of sequence stratigraphic interpretation, the lithofacies associations of the Irati Formation represent retrogradational, progradational and aggradational patterns (Milani 1998), which occur in three different fourth order cycles of relative sea level variations. According to this concept, the three depositional sequences of the Irati Formation were formed in transgressive and high system tracts settings (Araújo 2001).

## Methods

The characterization of inorganic components in black shales was made with X-ray fluorescence (EDXRF) to determine the elemental concentration, X-Ray diffraction (XRD) to determine the mineralogical components and scanning electron microscopy (EDX, BSE, SE) to determine the elemental modes of occurrence in the shales. Lixiviation and solubilization tests were also performed to estimate the potential of this shale as a font of fluoride registered in the groundwater of Guarani Aquifer.

## Sampling

Sample material was collected from outcrops, surface mines and core from exploration boreholes, provided by the Geological Survey of Brazil (CPRM) and the National Department of Mineral Production (DNPM). The study is based on an extensive sampling representing the whole area of outcrops occurrences of the Irati and Ponta Grossa formations along a SE–NW transect in the Brazilian



portion of the Paraná Basin (Fig. 2). The samples were collected as full interval channel samples, including parting. Following sampling the material was homogenized according to ASTM (1991) norm D2797 and split for the various analyses.

#### Solubilization/lixiviation tests

Solubilization and lixiviation tests were done in five samples (Table 5) of black shales of the Irati and Ponta Grossa Formations that presented fluorite in electronic microscopy analyses. The methodology applied for solubility/lixiviation tests are described below. Ten grams of crushed sample (smaller than 200 mesh) were added to 100 ml of distilled water in a closed PVC container. The mixture was stirred mechanically for 30 days for the solubilization of minerals. After this period, the pH was adjusted to a value next to 9.0. The solution was maintained at rest for 48 h for the decantation of solid particles and lixiviation of fluoride adsorbed in minerals and in organic matter. The solutions were then filtered and analyzed for determination of dissolved fluoride concentration. The dissolved fluoride was analyzed through visible spectrophotometry technique using a HACH DR-2010 machine. The content of fluoride extracted from sediments was, calculated by the equation:

$$F_{\text{mg/kg}} = F_{\text{mg/l}} \times Vs/Ma$$

$F_{\text{mg/kg}}$  is the mass (g) of fluoride extracted per kg of sediment sample;  $F_{\text{mg/l}}$  is the concentration of fluoride of the solution;  $Va$  is the volume of the solution (ml) and  $Ma$  is the mass of sample (g).

#### X-ray fluorescence (EDXRF)

The major oxides and trace elements were analyzed in Rigaku (RIX-2000) equipment–X-ray fluorescence spectrometry analyzer. The analysis of major oxides was done in glass bricket using 50 kV and 40 mA for a duration of 40 s and 10 s for pick and background lectures, respectively. The analysis of trace elements was done in pellets using 50 kV and 50 mA for a duration of 60 s and 10 s for pick and background lectures, respectively. For trace elements, corrections were done for matrix effects and pick interference.

#### X-ray diffraction (XRD)

X-ray powder diffraction patterns were obtained with an X-ray diffractometer (D5000 Siemens-Bruker-AXS, 40 kV, 25 mA, Cu  $K\alpha$  radiation, diffract plus<sup>®</sup> Siemens-Bruker-AXS software was used for data treatment). The

sampling of black shales was carried out with steps of 0.02° and its range was 2–72° in Bragg Brentano geometry.

The total mineralogy was analyzed in 22 samples of shales from Irati and Ponta Grossa formations, of which 6 samples were from Ponta Grossa Formation and 16 samples were from the Irati Formation.

#### Scanning electron microscopy (SEM)

The distribution of the elements in the black shales of Irati and Ponta Grossa Formations inorganic fractions was determined using scanning electron microscopy (SEM).

For the SEM, the following procedures were executed: The samples were fixed on a stub and carbon and gold coated, using a Sputter Coater (SCD 005/BALTEC) with approximately 20 nm of thickness, in order to eliminate any undesirable charge effects during SEM observations. After these procedures, it was possible to carry out the microscopy analysis. The instrument used in this study was standard Philips XL30 model. The images used in this work were obtained in back-scattered electron (BSE) and secondary electron (SE) mode, with a primary scanning beam of voltage of approximately 20 kV. Inorganic inclusions on the surface of source rocks specimens were analyzed using a SEM equipped with an energy dispersive X-ray (EDX) detector.

#### Petrography

In addition to chemical analysis, routine four samples of black shales were selected for petrographic analysis, which was carry out using binocular polarized microscope Leica DFC-280 with Sony 3CCD digital camera in thin sections and polished sections to identify the main mineral phases.

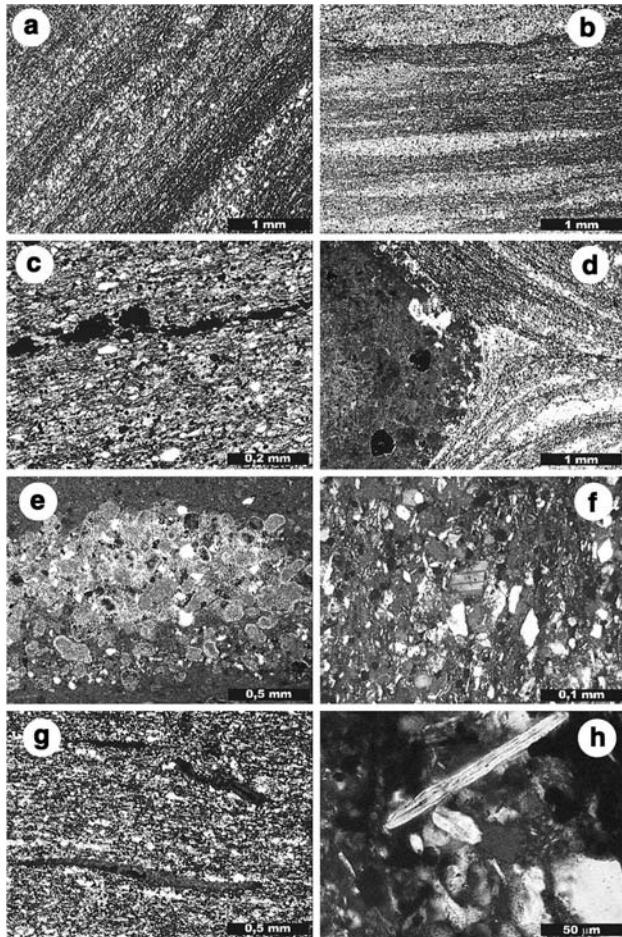
## Results and discussion

The techniques used in this work were applied to evaluate the nature of mineral matter. This study illustrates that the SEM techniques of back-scattered electron scanning (BSE) and microanalysis represent important tools in the field of organic geochemistry. It was possible by means of SEM to locate sedimentary organic matter in source rock and to directly analyze for elemental content using BSE and EDS.

#### Mineralogy

Irati and Ponta Grossa black shales are fine-grained clastic sedimentary rocks, with a mean grain size smaller than

65  $\mu\text{m}$  that are composed of organic matter, clay minerals (kaolinite and Illite), and contain subordinate amounts of quartz, plagioclase, carbonates (calcite, dolomite and ankerite), phosphate minerals, sulfides (pyrite) in some cases, barite, fluorite and rutile (Fig. 4). These shales usually show laminated bedding (Fig. 4a–c), sometimes deformed by volcanic clasts, ranging from less than



**Fig. 4** Photomicrography of thin sections showing the fabric, structures, textures and mineralogical composition of samples from Irati and Ponta Grossa Formations. **a** Plan parallel lamination and optical fissility typical of black shales from Irati Formation. **b** Laminar structure in samples of Ponta Grossa Formation. **c** Plan parallel lamination and quartz and pyrite crystals in organic matrix in Irati black shales. **d** Volcanic clast deforming the laminated structure in Irati black shales. **e** Thin section of calcilutite intercalated in black shale levels showing crystals of quartz, clay minerals and pyrite and organic matter fragments. **f** Main mineral phases in Irati black shales and a plagioclase crystal involved in diverse grains of quartz, clay minerals and opaque minerals. **g** Photomicrography of thin sections showing the fabric, structures, textures and mineralogical composition of black shale samples and diverse grains of quartz involved in a matrix composed of muscovite, lamellar smectite and pyrite. **h** Main mineral phases in Irati black shales and diverse grains of quartz involved in a matrix composed of muscovite, pyrite and very fine lamellar smectite

millimeters to 1 cm thickness (Fig. 4d). The diffractograms show general patterns in the main and more predominant mineralogy, seeking to illustrate the results of Irati (Fig. 5a) and Ponta Grossa (Fig. 5b) Formations.

The samples analyzed by SEM indicated that Ponta Grossa Formation present main mineralogy like quartz, illite/muscovite, kaolinite and pyrite.

In some samples, the presence of chlorite, K-feldspar, hematite, smectite and pirofilita was observed (Fig. 6). Irati black shales are, in its great majority, formed essentially for generally fine granulometry and constitute of clay-minerals, polymorphous silica, essentially quartz, K-feldspar, plagioclase, carbonates such as calcite, dolomite and ankerite, oxides such as rutile or anatase, sulfites such as pyrite (amorphous, framboidal and cubic crystalline form), sulfates such as barite, and phosphates such as apatite and fluorite (Fig. 7). These results are shown in Table 1.

#### Geochemical: Major oxides of shales

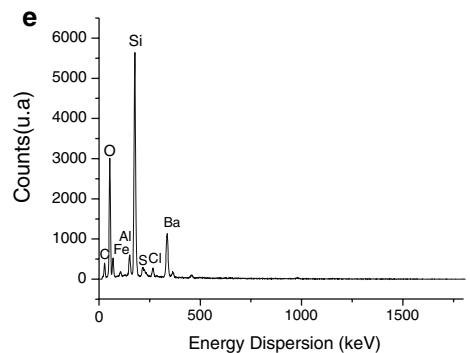
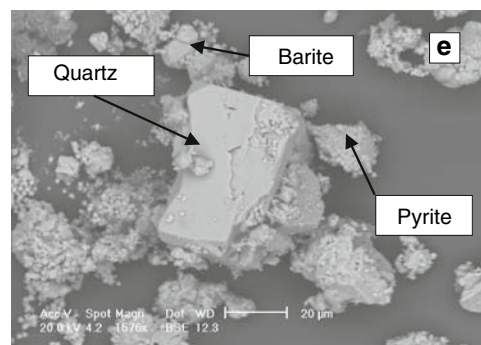
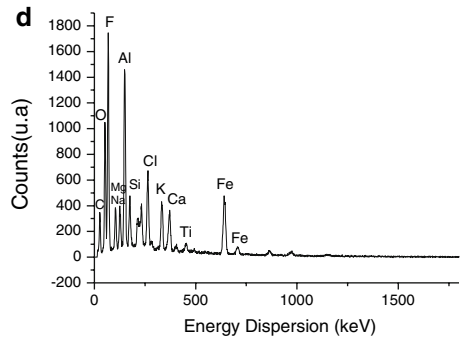
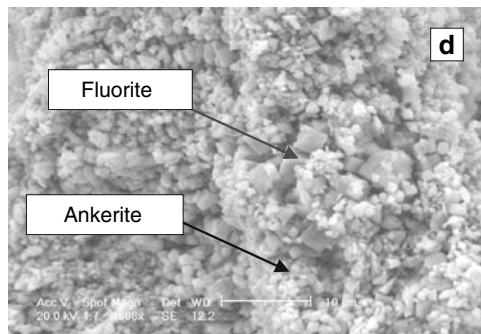
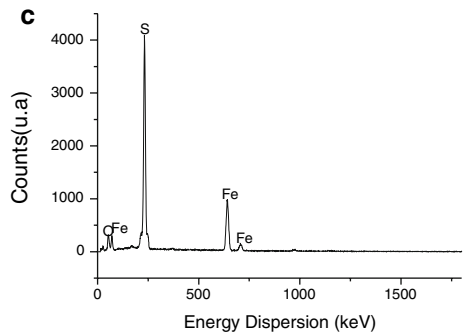
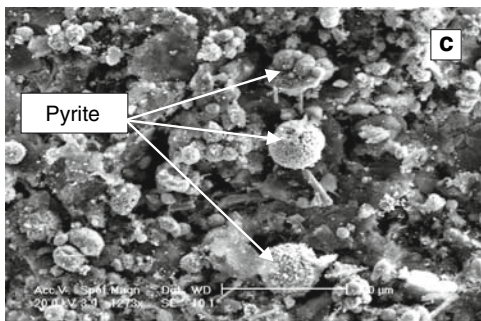
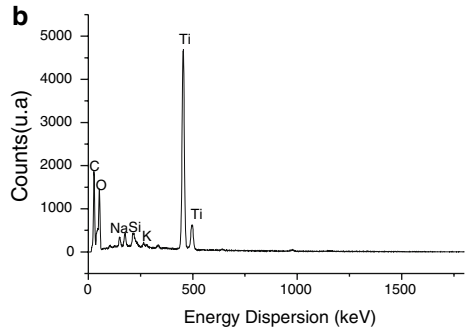
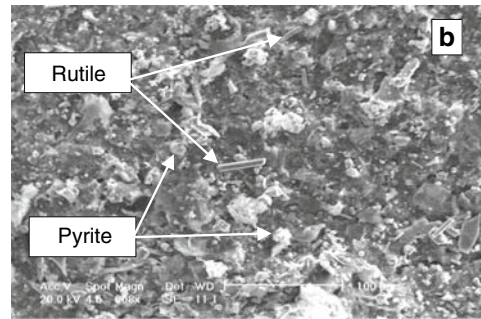
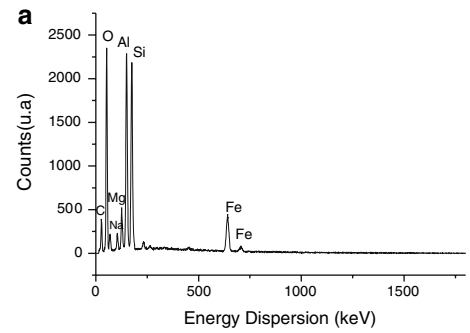
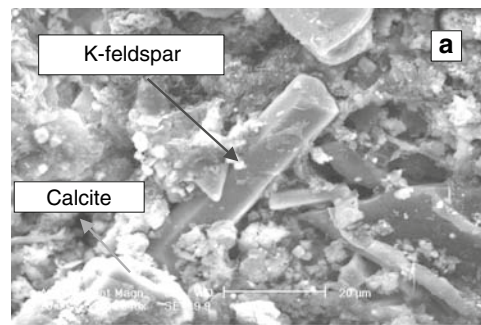
The major element distribution is based on whole black shales characteristics; on the other hand, the proportions of the different elements has been determined with the black shales using X-ray fluorescence (XRF) analysis that shows features of black shales of Irati and Ponta Grossa Formations, as can be observed in Table 2.

The identification of the different oxides by XFR methods shows that in Irati Formation, the black shales are richer in  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{P}_2\text{O}_5$  and  $\text{SO}_4$  than the Ponta Grossa black shales. On the other hand, Ponta Grossa black shales are richer in  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  and  $\text{K}_2\text{O}$ .

The range for total sulfur was 2.96–4.68 wt%, with an average of 3.82 wt%. The  $\text{Na}_2\text{O}$  percent in the Ponta Grossa black shales is very low, generally less than 0.32 wt% but Irati samples have more than 2.12 wt%  $\text{Na}_2\text{O}$ . The  $\text{Al}_2\text{O}_3$  content is relatively low in Irati samples, with many samples having less than 13.2 wt%, but in Ponta Grossa samples, the  $\text{Al}_2\text{O}_3$  content is larger than 25.2 wt%. These elevated  $\text{Al}_2\text{O}_3$  concentrations in Ponta Grossa Formation are the results of great quantity of clay minerals in these rocks.

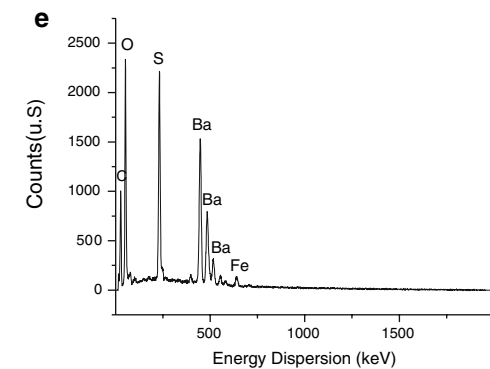
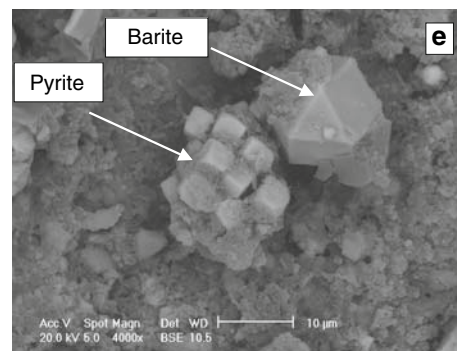
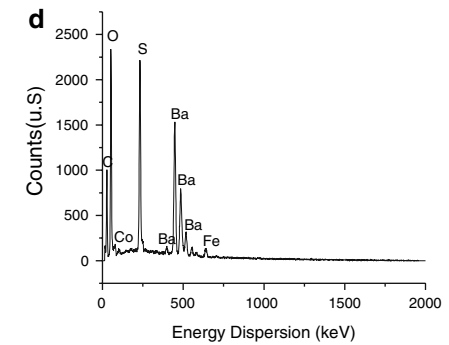
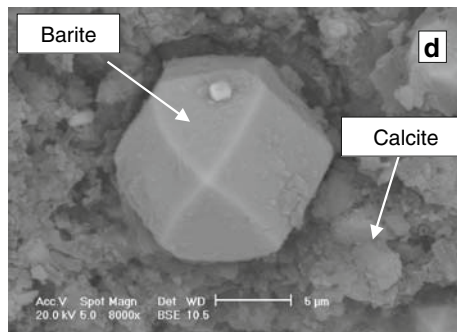
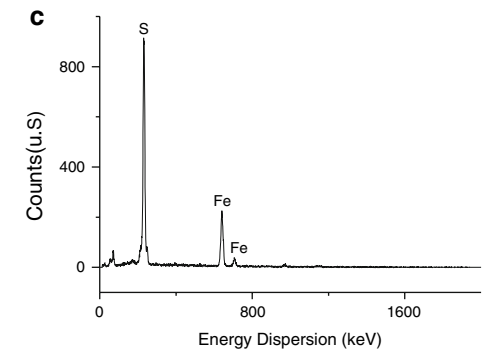
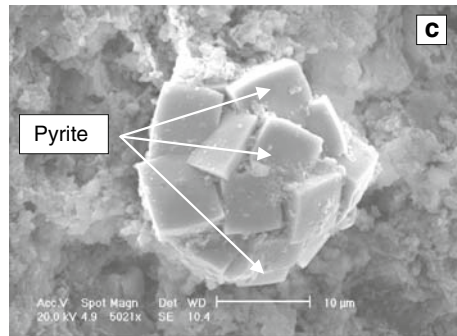
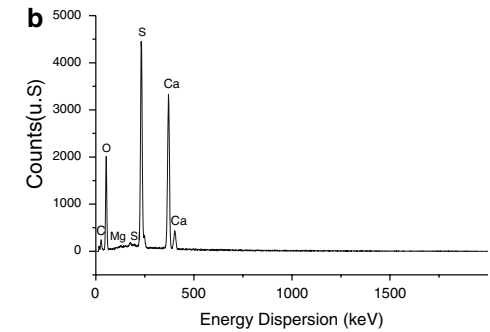
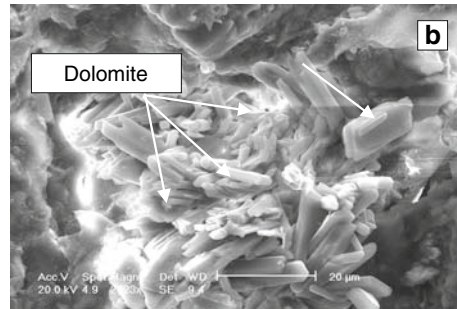
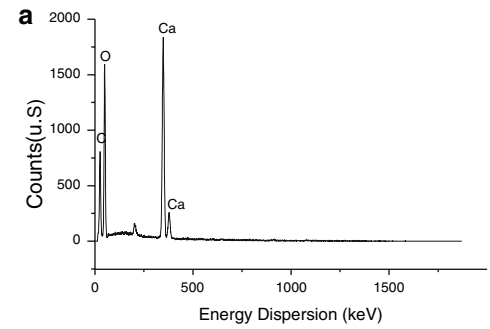
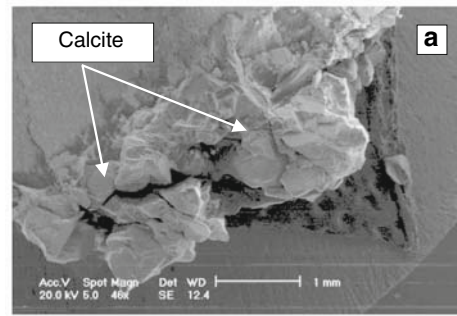
The  $\text{CaO}$  contents are very low in the Ponta Grossa samples, generally less than 0.03 and 1.66 wt% in Irati samples. The  $\text{Fe}_2\text{O}_3$  contents in Irati Formation present an average value of 4.17 up to 12.90 wt%. In Ponta Grossa Formation, the  $\text{Fe}_2\text{O}_3$  contents are highly variable ranging from 5.99 to 13.89 wt%. These elevated  $\text{Fe}_2\text{O}_3$  concentrations in Ponta Grossa Formation are the results of great quantity of pyrite in these rocks. The values of  $\text{K}_2\text{O}$  are low in the Irati samples, generally smaller than 2.26 wt% in Ponta Grossa Formation. The  $\text{SiO}_2$  content ranges from

**Fig. 5** Examples of samples of Ponta Grossa with SEM micrographs and X-ray characteristic (EDS), respectively, showing the morphology and identification of mineral content. **a** *K-Feldspar* and *Calcite* in sample 04-056. **b** *Rutile* and *Pyrite* in sample 04-079. **c** *Pyrite* in sample 04-077. **d** *Fluorite* and *Ankerite* in sample 04-079. **e** *Quartz*, *Barite* and *Pyrite* in sample 04-079

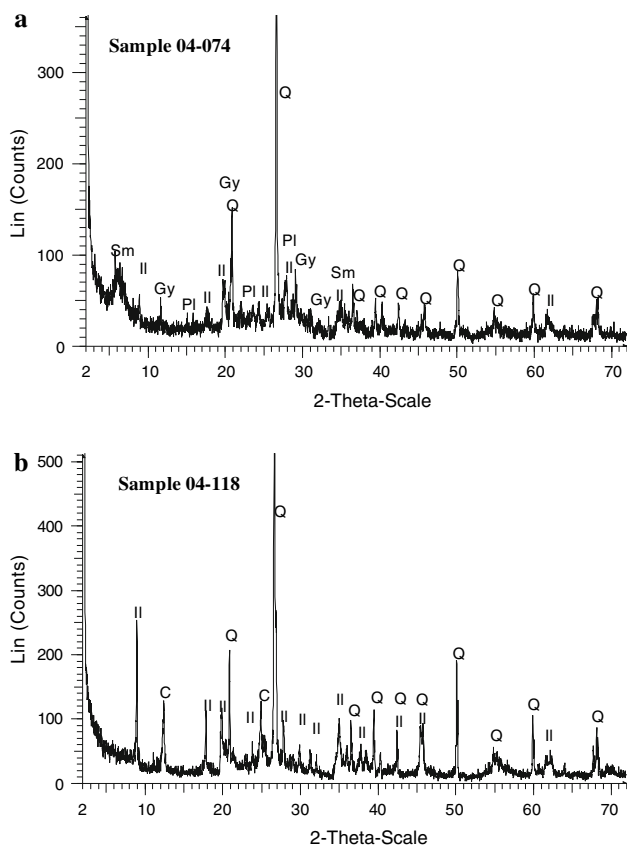




**Fig. 6** Examples of samples of Irati with SEM micrographs and X-ray characteristic (EDS), respectively, showing the morphology and identification of mineral content. **a** *Calcite* in sample 04-055. **b** *Calcite* and *Dolomite* in sample 04-049. **c** *Pyrite* in sample 04-166. **d** *Barite* in sample 04-165. **e** *Barite* and *Pyrite* in sample 04-165







**Fig. 7** **a** Illustrative diffractogram of sample from Ponta Grossa Formation (sample 04-074). The figure shows the main mineralogy of the shale analyzed. *Q* quartz, *Il* Illite, *Gy* gypsum, *Sm* smectite, *Pl* plagioclase. **b** Illustrative diffractogram of sample from Irati Formation (sample 04-118) *Q* quartz, *Il* illite, *K* kaolinite. The figure shows the main mineralogy of the shale analyzed

60.17 wt% in Irati samples to 57.3 wt% in Ponta Grossa samples.

The X-Ray fluorescence analysis confirms the high content of SiO<sub>2</sub> in the black shales and the relatively low MgO, MnO and TiO<sub>2</sub> contents with average values of 1.01, 0.02 and 0.03 wt%, respectively, for Ponta Grossa Formation. In the Irati Formation, these vales are 1.03, 0.03 and 0.14 wt%, respectively.

Geochemical: Trace elements of shales

Irati and Ponta Grossa black shales present chemical compositions characterized by high plumbum (up to 780 ppm) and barium (up to 769 ppm) concentrations. The sample concentrations of major oxides and trace elements are presented in Tables 2 and 3, respectively. A comparison of average concentration of Irati and Ponta Grossa Formation with other black shales from other parts of the

world is presented in Table 4. The data presented in this table shows that Irati and Ponta Grossa Formations have higher concentrations of Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Ba and Pb than black shales from others sedimentary basins. On the other hand, the average concentrations of Mo, V, Ni, Zn, Y, P and Mn are lower, wile the concentrations of Cr, Cu, Co, Sr, Nb, Rb, Ga, Ag, Cd and As are similar when compared with other black shales (Leventhal 1993. In: Engel and Macko 1993).

Geochemical: Fluoride solubilization and lixiviation of shales

Microcrystals of fluorite occur frequently dispersed in the matrix of Irati and Ponta Grossa Formations (Fig. 5d). The solubilization of this fluorite can be the most important source of the fluoride dissolved in groundwater of Guarani Aquifer. Solubilization and lixiviation tests were done in samples from the black shales of the Irati and Ponta Grossa Formations. The resultant solutions of these experiments showed high contents of dissolved fluoride. The results obtained indicate solubilization and lixiviation of 8.6–21.80 mg of fluoride per kg of sediment. The concentration of fluoride in the solutions obtained in the solubilization/lixiviation tests present good positive correlation with the content of organic matter in the black shales (Table 4; Fig. 8). This means that the dissolved fluoride is more enriched in groundwaters that circulate through the black shales with higher content of organic matter (Table 5).

The results demonstrate that the black shales can be the main source of the high fluoride content in the groundwater of Guarani Aquifer System. The incorporation of fluoride into the groundwater of Guarani Aquifer is related to deep circulation mechanisms of the groundwater that ascend from the underlying packages of the Paraná Basin through regional faults and fractures. These regional structures are identified and described by many authors, such as Zalán et al. (1990), Milani (1998) and Machado (2006).

Conclusions

This work suggests that the fluoride present in groundwater of Guarani Aquifer results mainly from water that circulates in deeper seams such as Ponta Grossa and Irati Formations. This promotes the dissolution of fluorite and lixiviation of fluoride resulting in anomalous concentrations of this ion in the groundwater from many locales of the aquifer.

The content of V, Mo, Cd and B in the Ponta Grossa Formation shales are low. Regarding the Irati shales, they

**Table 1** The mineral phases present in the analyzed shales from Irati and Ponta Grossa formations

Samples	Formation	Quartz	Illite/ Muscovite	Smectite	Kaolinite	Chlorite	Gibbsite	Calcite	Dolomite	Ankerite	Chistobalite	Gypsum	Hematite
1	Irati	×	×	×	×							×	
2	Irati	×	×			×					×		
3	Irati	×	×		×							×	
4	Pta. Grossa	×	×		×	×							
5	Pta. Grossa	×	×		×								×
6	Pta. Grossa	×	×		×	×							
7	Pta. Grossa	×	×	×	×								
8	Pta. Grossa	×	×		×								
9	Irati	×	×		×								
10	Irati	×	×		×								
11	Irati	×	×	×								×	
12	Irati	×	×		×								
13	Irati	×	×					×				×	
14	Irati	×	×		×	×							
15	Irati	×	×		×	×							
16	Irati	×	×	×				×				×	
17	Irati	×	×	×								×	
18	Irati	×	×	×				×				×	
19	Irati	×		×								×	
20	Irati	×		×	×			×					
21	Irati	×	×		×					×			
22	Irati	×	×	×									

Samples	Formation	Talc	Pyroxene	Pirrotite	Plagioclase	K-feldspar	Pirophillite	Pyrite	Rutile/Anatase	Apatite	Barite	Fluorite
1	Irati				×			×	×			
2	Irati				×			×				
3	Irati				×			×				×
4	Pta. Grossa							×				
5	Pta. Grossa							×				×
6	Pta. Grossa							×				
7	Pta. Grossa							×				×
8	Pta. Grossa							×				
9	Irati			×	×			×				×
10	Irati											
11	Irati				×				×			
12	Irati				×			×		×	×	
13	Irati				×						×	
14	Irati				×					×	×	
15	Irati			×	×			×			×	
16	Irati				×							
17	Irati	×			×			×				
18	Irati		×		×							
19	Irati							×				
20	Irati	×										
21	Irati					×		×	×			
22	Irati								×			

**Table 2** Major constituents of black shales samples from Irati and Ponta Grossa formations

Samples	Geologic unity	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO	CaO
1	Pta. Grossa	57.81	22.88	7.97	3.49	1.89	0.03
2	Pta. Grossa	55.41	21.19	6.11	3.93	1.80	1.57
3	Pta. Grossa	59.08	25.08	5.99	4.67	1.74	2.03
4	Pta. Grossa	51.07	24.01	13.89	1.71	1.49	4.75
5	Pta. Grossa	56.81	27.53	5.33	3.63	1.07	0.04
6	Pta. Grossa	58.63	27.35	3.05	3.21	1.02	0.03
7	Irati	56.38	13.64	12.9	2.86	2.15	1.58
8	Irati	63.96	17.29	8.28	2.52	1.68	2.24
9	Irati	58.10	17.11	5.62	3.21	1.40	1.51
10	Irati	59.03	16.89	8.30	4.76	1.43	1.78
11	Irati	58.04	25.95	3.96	2.51	1.67	2.89
12	Irati	57.09	26.01	4.64	3.71	1.42	1.75
13	Irati	58.85	26.70	6.08	2.95	1.40	1.58
14	Irati	57.32	26.89	4.13	1.31	1.03	1.33
15	Irati	66.11	17.01	6.01	3.01	1.04	1.04
16	Irati	58.39	18.20	8.99	3.15	1.05	1.03
17	Irati	55.41	28.60	3.45	2.71	1.01	1.07
18	Irati	59.25	17.25	4.89	2.61	0.99	1.95
19	Irati	56.75	23.39	2.75	1.46	1.01	1.45
20	Irati	59.35	27.01	4.31	0.56	1.05	1.46
21	Irati	59.45	18.02	1.76	0.34	1.03	8.73
22	Irati	59.18	25.43	2.87	0.53	1.01	0.68
Mean	Pta. Grossa	56.47	24.67	7.06	3.44	1.50	1.41
Mean	Irati	54.71	21.47	4.61	2.20	1.11	1.88

Samples	Geologic unity	Na <sub>2</sub> O	TiO <sub>2</sub>	MnO	P <sub>2</sub> O <sub>5</sub>	SO <sub>4</sub>	Loi
1	Pta. Grossa	0.18	1.03	0.03	0.05	–	4.64
2	Pta. Grossa	0.91	0.07	0.01	0.07	0.15	8.78
3	Pta. Grossa	0.45	0.06	0.02	0.05	0.78	0.05
4	Pta. Grossa	1.04	0.05	0.02	0.34	1.15	0.48
5	Pta. Grossa	0.45	1.03	0.01	0.03	–	4.07
6	Pta. Grossa	0.81	0.07	0.09	0.05	2.74	2.95
7	Irati	1.42	0.72	0.03	0.03	4.68	3.61
8	Irati	1.46	0.56	0.06	0.03	2.96	9.76
9	Irati	1.51	0.03	0.03	0.03	2.81	8.64
10	Irati	1.05	0.47	0.02	0.03	1.02	5.22
11	Irati	1.03	0.25	0.02	0.03	0.89	2.76
12	Irati	0.99	0.37	0.01	0.02	–	3.99
13	Irati	0.12	0.29	0.02	0.05	0.12	1.84
14	Irati	0.81	0.13	0.04	0.03	1.25	5.73
15	Irati	0.20	0.05	0.05	0.03	0.45	5.00
16	Irati	0.80	0.32	0.04	0.02	2.11	5.90
17	Irati	0.73	0.27	0.01	0.03	4.85	1.86
18	Irati	0.74	0.03	0.05	0.02	3.5	8.72
19	Irati	0.75	0.09	0.02	0.04	1.90	10.39
20	Irati	0.77	0.01	0.06	0.02	2.15	3.25
21	Irati	0.78	0.02	0.05	0.01	3.01	6.80
22	Irati	0.91	0.02	0.04	0.01	3.01	6.31
Mean	Pta. Grossa	0.64	0.39	0.03	0.10	0.80	3.50
Mean	Irati	0.69	0.18	0.03	0.03	1.67	4.75



**Table 3** Traces elements of black shales samples from Irati (I) and Ponta Grossa (PG)

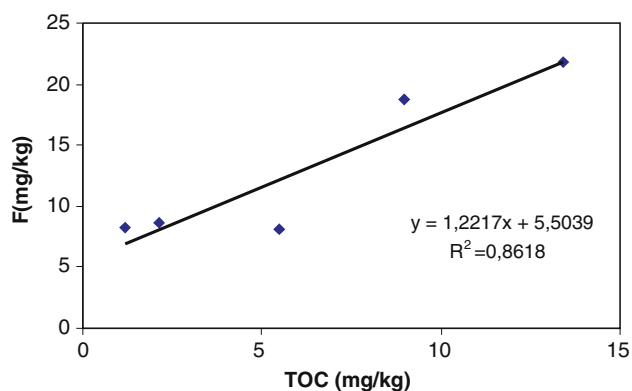
Sample	Geologic unity	Y	Pb	Ni	Co	Cu	Ga	Sr	Zr	Zn
1	Pta. Grossa	23	91	45	22	30	21	88	188	59
2	Pta. Grossa	97	684	37	–	75	–	196	315	–
3	Pta. Grossa	62	531	67	–	74	–	213	329	–
4	Pta. Grossa	84	3,420	94	–	168	–	237	323	–
5	Pta. Grossa	35	115	22	1	27	26	145	212	29
6	Pta. Grossa	58	555	43	–	77	–	133	442	–
7	Irati	100	38	38	89	106	27	198	168	246
8	Irati	20	55	18	25	62	11	195	185	79
9	Irati	44	35	27	28	128	17	113	164	140
10	Irati	46	33	271	45	169	23	419	183	109
11	Irati	56	229	47	–	67	–	376	345	–
12	Irati	–	217	34	23	61	–	509	389	71
13	Irati	35	39	26	34	113	16	87	123	119
14	Irati	–	317	27	30	76	–	407	178	25
15	Irati	–	315	25	–	71	–	181	201	–
16	Irati	76	263	31	25	86	–	234	363	–
17	Irati	–	234	74	–	69	–	749	272	50
18	Irati	43	157	105	5	67	–	281	408	21
19	Irati	54	375	110	15	48	–	462	185	69
20	Irati	–	137	13	–	37	–	236	169	–
21	Irati	–	126	–	–	35	–	103	346	–
22	Irati	35	180	86	103	173	20	107	175	51
Mean	Irati	51	172	58	39	85	19	291	241	89
Mean	Pta. Grossa	60	780	48	13	72	29	170	293	50
Sample	Geologic unity	Nb	Rb	As	Cr	Ba	V	B	Mo	Cd
1	Pta. Grossa	18	156	13	186	571	210	17	5	5
2	Pta. Grossa	–	309	310	86	601	–	–	–	–
3	Pta. Grossa	–	355	355	430	–	–	–	–	–
4	Pta. Grossa	–	95	723	479	741	–	–	–	–
5	Pta. Grossa	19	184	19	191	723	140	20	10	1
6	Pta. Grossa	–	220	117	325	–	–	–	–	–
7	Irati	32	290	59	286	631	140	65	9	2
8	Irati	11	103	18	103	743	70	15	11	3
9	Irati	17	69	22	100	414	–	–	–	–
10	Irati	20	223	21	141	721	–	–	–	–
11	Irati	–	267	48	251	–	–	–	–	–
12	Irati	–	273	47	221	–	120	42	11	3
13	Irati	15	146	21	422	385	–	56	13	5
14	Irati	–	103	67	230	–	105	30	10	4
15	Irati	–	91	49	135	–	–	–	15	3
16	Irati	–	260	55	352	–	753	25	10	5
17	Irati	–	165	49	214	–	70	52	13	2
18	Irati	–	207	32	255	–	–	15	–	–
19	Irati	–	56	80	145	–	70	30	5	1
20	Irati	–	35	28	112	–	–	–	–	–
21	Irati	–	16	27	138	–	–	–	–	–
22	Irati	20	69	174	142	1,720	–	–	–	–
Mean	Irati	19	148	50	203	769	190	37	11	3
Mean	Pta. Grossa	25	231	224	297	685	175	19	8	3

**Table 4** Representative element values for selected shale units from Leventhal (1993) modified and average data obtained from Ponta Grossa and Irati shales

Shales	Al (%)	Fe (%)	S (%)	C (%)	U (ppm)	Mo (ppm)	V (ppm)	Ni (ppm)	Cu (ppm)	Cr (ppm)	Co (ppm)	As (ppm)	Pb (ppm)
Atlantic Cretaceous	–	3.5	1.3	6.2	–	60	820	190	160	200	30	–	16
Green River Eocene Fm	–	2	1.6	30	10	30	150	30	70	40	10	35	40
Black Sea Layer C	–	3.8	1.6	3.5	12	25	250	100	55	150	–	–	11
Appalachian Devonian	–	4	3	10	60	90	300	150	150	60	25	60	30
Condor Australia	–	4.6	0.7	11.7	1	30	110	25	25	55	15	9	–
Alum Cambrian	–	7.1	6.7	13.7	206	270	680	160	190	94	50	17	140
Kolm from Alum	6	6	7.7	50	4,500	90	290	95	60	–	–	150	230
Mecca Quarry Pennsylvanian	–	3.6	3	30	130	1,100	1,800	400	100	400	–	30	30
New Albany Devonian	7	2	1.6	8.4	11	15	200	50	150	70	15	17	15
Falling run Henryville	–	4.5	3	17	125	70	1,000	200	300	100	5	–	150
Ponta Grossa Devonian	22	8	5.5	1.8	–	7	175	53	75	186	11	46	968
Irati Permian	13	13	4.7	21	–	10	321	62	72	140	57	51	260

Shales	Ba (ppm)	Zn (ppm)	Ag (ppm)	Cd (ppm)	Ree + Y (ppm)	P (ppm)	Mn (ppm)	Sr (ppm)	Nb (ppm)	Rb (ppm)	Ga (ppm)	Ca (%)	Carbonate (%)
Atlantic Cretaceous	530	830	4.5	0.9	–	–	910	–	–	–	–	–	–
Green River Eocene Fm	300	–	–	1	–	–	220	–	–	–	–	–	–
Black Sea Layer C	–	108	–	–	–	–	–	–	–	–	–	–	1.7
Appalachian Devonian	400	200	0.2	–	150	–	100	–	–	–	–	–	–
Condor Australia	200	65	–	–	–	–	350	–	–	–	–	0.4	0.6
Alum Cambrian	500	150	1	–	200	500	–	–	–	–	–	–	–
Kolm from Alum	400	200	–	3	1,300	500	240	–	–	–	–	–	–
Mecca Quarry Pennsylvanian	300	1,500	–	70	150	4,000	250	–	–	–	–	1	0.1
New Albany Devonian	700	<300	<0.2	<1	–	–	200	–	–	–	–	1.5	0.8
Falling run Henryville	300	1,000	–	–	6	2%	50	–	–	–	–	2.8	0.4
Ponta Grossa Devonian	659	44	–	3	60	2	0.3	176	18	220	23	1.9	0.3
Irati Permian	671	162	–	2	55	4	0.3	318	21	172	19	1.2	1.5



**Fig. 8** Correlation diagram for F versus TOC showing high affinity of the fluoride and organic matter

**Table 5** Geochemical: fluoride solubilization and lixiviation of black shales

Sample	pH solution after 30 days	Adjusted pH of solution	F in the solution (mg/l)	F extracted of black shales (mg/kg)	TOC in black shales (mg/kg)
04-049	3.0	9.0	1.88	18.80	8.98
04-055	5.0	8.5	2.18	21.80	13.40
04-074	2.5	9.0	0.83	8.30	1.19
04-116	6.0	9.0	0.86	8.60	2.11
04-165	6.0	9.0	0.81	8.10	5.49

can be described as the ones that showed higher contents of Y, Ga, Ni, Co, Cu, Sr, Zn, Nb, Rb, Cr, Ba, As and Zr.

The mineralogy of the black shales from the formations of Irati and Ponta Grossa is constituted essentially of quartz, illite, muscovite, kaolinite and smectite, and great amounts of organic matter. Plagioclase, calcite, dolomite, ankerite, apatite, pyrite, barite, fluorite and rutile are also registered. The fluorite appears frequently as cubic diagenetic microcrystals, identified only in the MEV analyses that normally associate with the organic matter.

The chemical composition of these black shales is characterized by the high contents of  $Al_2O_3$  and  $Fe_2O_3$  and low content of CaO, and associated with the organic matter, high contents of Pb, Ni, Co, Cu, Zr, Cr, Ba and V were registered.

The high content of microcrystalline fluorite in black shales allows the solubility and leaching of great amounts of fluoride from them, which are characterized as a potential source of high fluoride concentrations registered in the groundwater of Guarani Aquifer System. The interaction of the groundwater circulating in the deep black shales with groundwater from Guarani Aquifer System occurs through great faults and tectonic lineaments that constitute excellent hydraulic connectors between the two sedimentary packages.

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