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Fluoride geochemistry of thermal waters in Yellowstone National Park: I. Aqueous fluoride speciation

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Abstract

Thermal water samples from Yellowstone National Park (YNP) have a wide range of pH (1–10), temperature, and high concentrations of fluoride (up to 50 mg/l). High fluoride concentrations are found in waters with field pH higher than 6 (except those in Crater Hills) and temperatures higher than 50 °C based on data from more than 750 water samples covering most thermal areas in YNP from 1975 to 2008. In this study, more than 140 water samples from YNP collected in 2006–2009 were analyzed for free-fluoride activity by ion-selective electrode (ISE) method as an independent check on the reliability of fluoride speciation calculations. The free to total fluoride concentration ratio ranged from <1% at low pH values to >99% at high pH. The wide range in fluoride activity can be explained by strong complexing with H^+ and Al^{3+} under acidic conditions and lack of complexing under basic conditions. Differences between the free-fluoride activities calculated with the WATEQ4F code and those measured by ISE were within 0.3–30% for more than 90% of samples at or above 10^{-6} molar, providing corroboration for chemical speciation models for a wide range of pH and chemistry of YNP thermal waters. Calculated speciation results show that free fluoride, F^-, and major complexes ($HF^0_{(aq)}$, AlF^{2+}, AlF_2^+ and AlF_3^0) account for more than 95% of total fluoride. Occasionally, some complex species like AlF_4^-, FeF^{2+}, FeF_2^+, MgF^+ and $BF_2(OH)_2^-$ may comprise 1–10% when the concentrations of the appropriate components are high. According to the simulation results by PHREEQC and calculated results, the ratio of main fluoride species to total fluoride varies as a function of pH and the concentrations and ratios of F and Al.
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1. INTRODUCTION

Fluorine is the lightest element of the halogen group, the most electronegative, and the most reactive of all the chemical elements (Pauling, 1970, p. 217). Fluoride is not only an important component in natural waters in relation to metal complexation, but an essential element for life with the optimal concentration in a narrow range between beneficial intake and toxic exposure. It is generally believed that fluoride deficiencies can arise at low concentration, but at high fluoride concentrations other detrimental effects can occur such as dental and skeletal fluorosis (Edmunds and Smedley, 2005). Most previous studies on the aqueous geochemistry of fluoride were focused on factors controlling fluoride enrichment in groundwater because a huge population across the world has suffered from endemic fluorosis because of long-term ingestion of high-fluoride groundwater (Edmunds and Smedley, 2005; Kim and Jeong, 2005; Jacks et al., 2005; Chae et al., 2007). The maximum concentration of fluoride in groundwater is often controlled by the solubility of fluorite (Nordstrom and Jenne, 1977; Edmunds and Smedley, 2005) and associated with high pH in sodium-bicarbonate type waters (Cederstrom, 1946; Foster, 1950; Zack, 1980), or hydrothermal waters, especially in arid and semiarid environments (Nordstrom and Jenne, 1977; Reardon and Wang, 2000; Smedley et al., 2002; Edmunds and Smedley, 2005; Chae et al., 2007; Ozsvath, 2009; Wang et al., 2009). Besides fluorite, fluorapatite is also known to be a natural mineral source of fluoride in groundwater.

It is important for fluoride concentrations to be determined as part of comprehensive groundwater chemistry

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surveys and studies. Routine techniques for fluoride concentration determination in waters include fluoride ion-selective electrode (ISE) and ion-chromatography (IC). The fluoride ISE, a solid-state electrode, was originally found to be a robust, highly sensitive technique that responded with Nernstian quantitation to the activity of free fluoride (Frant and Ross, 1966; Butler, 1969; Daghetti and Tasatti, 1981). The linear working range becomes nonlinear at or below 10^{-6} m (limited by the solubility of LaF_3) although lower concentrations are still measurable (Barnard and Nordstrom, 1982). Although simple standard procedures have been developed for the fluoride ISE method (Midgley and Torrance, 1991), it is not as widely used as the IC method. Fluoride concentrations determined by ion chromatography are susceptible to errors from the "water dip," a dilution of the eluent at the leading edge of the injection, and from overlapping organic-acid peaks, such as formate, and shifts in retention times caused by high concentrations of Cl or SO_4 (Ball et al., 2006; Noh and Coetzee, 2006).

Fluoride ion, as a strong ligand in water, can form a series of soluble complexes with polyvalent cations such as magnesium (Mg^{2+}), iron (Fe^{3+}), aluminum (Al^{3+}), and calcium(Ca^{2+}) depending upon the pH of the medium (Nordstrom and Jenne, 1977). Fluoride also forms strong complexes with minor components such as boron, beryllium, silica, uranium, vanadium, and REEs (Hem, 1985; Lewis et al., 1998; Serrano et al., 2000). Because of the low concentrations of iron and aluminum in neutral waters, fluoride would not be bound to those cations to any significant extent. Therefore, free fluoride is generally the predominant species of fluorine in most natural waters, with minor amounts of complexes occurring with major cations and some minor or trace constituents (Edmunds and Smedley, 2005; Ozsvath, 2009). A few previous studies only determined concentrations of free fluoride ion in rain water (Barnard and Nordstrom, 1982; Hara et al., 1998), thermal waters (Nordstrom, 2001), and aqueous suspensions of montmorillonite and kaolinite (Agarwai et al., 2002). Little attention has been given to fluoride speciation analysis except by aqueous speciation calculations using geochemical modeling codes. Although aqueous speciation models have been used extensively to interpret water–rock interactions, reactive-transport processes, and solute–biota interactions (Nordstrom and Munoz, 1994; Langmuir, 1997), little work has been done to evaluate their reliability (Nordstrom and Ball, 1989; Nordstrom, 1996). In fact, different techniques used for the determination of inorganic or organic speciation often give varying results (Temminghoff et al., 2000; Nordstrom, 2004), and analytically derived speciation results have seldom been compared with computed results (Nordstrom, 1996).

Hydrothermal chemistry at Yellowstone National Park (YNP) was first documented by Gooch and Whitfield (1888) during the Hague expeditions of 1883–1886 (Fournier, 2005; Rodman and Guiles, 2008). The thermal activity is unique among presently active systems in regard to its unparalleled geysers, tectonic environment, and magnitude of volcanic activity (Fournier, 2005). Investigations into the water chemistry of hot springs, geysers, streams, and rivers in YNP have been conducted by the US Geological Survey (USGS) and others since 1888 (Ball et al., 2006). Hydrothermal waters undergoing rapid decreases in temperature and pressure and discharging to ground surface provide a wide variety of water chemistry and chemical and biological transformations which accompany these physical changes (Nordstrom et al., 2005). Hydrothermal water samples from Yellowstone have a wide range of pH (1–10), temperature, and water composition (Nordstrom, 2001; Ball et al., 2001, 2002, 2006; McCleskey et al., 2005), which offer an opportunity to study the geochemistry and speciation of fluoride in hydrothermal systems.

This paper is our first in a series on the geochemistry of fluoride in Yellowstone National Park using a greatly expanded analytical database with improved QA/QC (quality assurance/quality control) and a major update since our earlier publication (Nordstrom and Jenne, 1977). This paper focuses on aqueous fluoride speciation and a comparison between free fluoride-ion activities measured with the fluoride ISE and those computed with the WATEQ4F

Table 1

Thermodynamic data in the WATEQ4F code for modeling aqueous speciation and mineral solubility of fluoride species; $\Delta H°$, enthalpy of reaction under standard-state conditions (25 °C, 1 bar pressure, in kilocalories per mole; Log K, logarithm of the equilibrium constant for the reaction.

Aqueous species	Reaction	ΔH	Log K	Reference
MgF^+	$Mg^{2+} + F^- \leftrightarrows MgF^+$	3.2	1.82	Nordstrom and others (1990)
CaF^+	$Ca^{2+} + F^- \leftrightarrows CaF^+$	4.12	0.94	Nordstrom and others (1990)
$NaF°$	$Na^+ + F^- \leftrightarrows NaF°$	0	−0.24	Nordstrom and others (1990)
AlF_2^+	$Al^{3+} + F^- \leftrightarrows AlF^{2+}$	1.06	7.0	Nordstrom and May (1996)
AlF_2^+	$Al^{3+} + 2F^- \leftrightarrows AlF_2^+$	1.98	12.7	Nordstrom and May (1996)
$AlF_3°$	$Al^{3+} + 3F^- \leftrightarrows AlF_3°$	2.16	16.8	Nordstrom and May (1996)
AlF_4^-	$Al^{3+} + 4F^- \leftrightarrows AlF_4^-$	2.2	19.4	Nordstrom and May (1996)
FeF^{2+}	$Fe^{3+} + F^- \leftrightarrows FeF^{2+}$	2.7	6.2	Nordstrom and others (1990)
FeF_2^+	$Fe^{3+} + 2F^- \leftrightarrows FeF_2^+$	4.8	10.8	Nordstrom and others (1990)
$FeF_3°$	$Fe^{3+} + 3F^- \leftrightarrows FeF_3°$	5.4	14	Nordstrom and others (1990)
SiF_6^-	$H_4SiO_4° + 4H^+ + 6F^- \leftrightarrows SiF_6^{2-} + 4H_2O$	−16.26	30.18	Ball and Nordstrom (1991)
$HF°$	$H^+ + F^- \leftrightarrows HF°$ Log $KHF° = -2.033 + 0.012645T + 429.01/T$	3.18	3.18	Nordstrom and others (1990)
HF_2^-	$H^+ + 2F^- \leftrightarrows HF_2^-$	4.55	3.76	Nordstrom and others (1990)
$H_2F_2°$	$2H^+ + 2F^- \leftrightarrows H_2F_2°$	0	6.768	Ball and Nordstrom (1991)

Table 2
Chemical compositions and aqueous fluoride species distribution of selected geothermal waters in Yellowstone National Park (2006–2008).

Sample location	Units	Sulfur Caldron	Lifeboat Spring	Tantalus Creek	Sulphur Spring	Cinder Pool	Beryl Spring	Ojo Caliente
Sampling date		9/19/08	9/13/07	9/14/06	9/19/08	9/12/07	5/17/06	9/16/06
Temperature	°C	73.2	69.4	23.6	87.5	86.8	90.7	91.4
pH (field/lab)		1.60/1.58	2.48/2.39	3.02/3.02	3.75/3.46	4.28/3.96	6.71/8.22	7.52/8.33
SC	μS/cm	6640	2550	2290	3440	2090	2040	1495
Eh	V	nd	0.124	nd	0.11	−0.042	−0.030	nd
Ca	mg/L	36.8	4.19	4.09	5.63	5.22	3.67	0.867
Mg	mg/L	9.12	0.264	0.231	0.3	0.020	0.012	<0.007
Na	mg/L	317	282	310	576	409	409	323
K	mg/L	8.91	35.9	56.3	117	41.4	17.5	9.18
SO_4	mg/L	3490	405	155	425	63.7	62.2	21.6
H_2S	mg/L	nd	0.08	nd	1.03	2.12	0.39	0.96
HCO_3	mg/L	nd	nd	nd	nd	nd	97	232
Cl	mg/L	2.86	412	490	802	633	523	318
F	mg/L	4.45	3.36	4.27	48.6	6.83	17.1	34.5
NH_4-N	mg/L	86.6	1.8	1.4	16.8	6.77	0.697	<0.07
SiO_2	mg/L	291	369	364	743	383	46.1	257
B	mg/L	3.28	5.98	7.63	23.5	9.7	7.14	4.13
Al	mg/L	81.6	2.86	2.47	5.92	0.95	0.16	0.26
Fe	mg/L	20.4	37.1	1.27	0.141	0.012	<0.002	0.007
As	mg/L	0.0037	14.6	1.85	5.57	2.35	2.90	1.43
Charge imbalance	%	8.2	3.6	−0.2	−5.3	3.7	2.9	−1.4
Free F^-	%	0.04	1.66	6.63	39.81	59.02	98.94	99.32
$HF^0_{(aq)}$	%	2.77	16.59	8.07	29.87	13.5	0.09	0.01
AlF^{2+}	%	93.08	27.17	6.77		0.04		
AlF_2^+	%	4.08	52.36	58.97	1.24	6.06		
AlF_3^0	%		2.2	12.66	16.87	18.56	0.02	0
AlF_4^-	%			0.1	9.32	2.13	0.01	0
FeF^{2+}	%	0.03		3.96				
FeF_2^+	%			2.72				
FeF_3^0	%			0.07				
NaF^0	%		0.01	0.04	0.38	0.44	0.74	0.60
$BF(OH)_3^-$	%				0.06	0.04	0.05	0.03
$BF_2(OH)_2^-$	%				1.76	0.07		
$BF_3(OH)^-$	%				0.17			
CaF^+	%				0.06	0.11	0.14	0.03
MgF^+	%				0.02			
SiF_6^{2-}	%				0.03			

SC: specific conductance; nd: not determined.

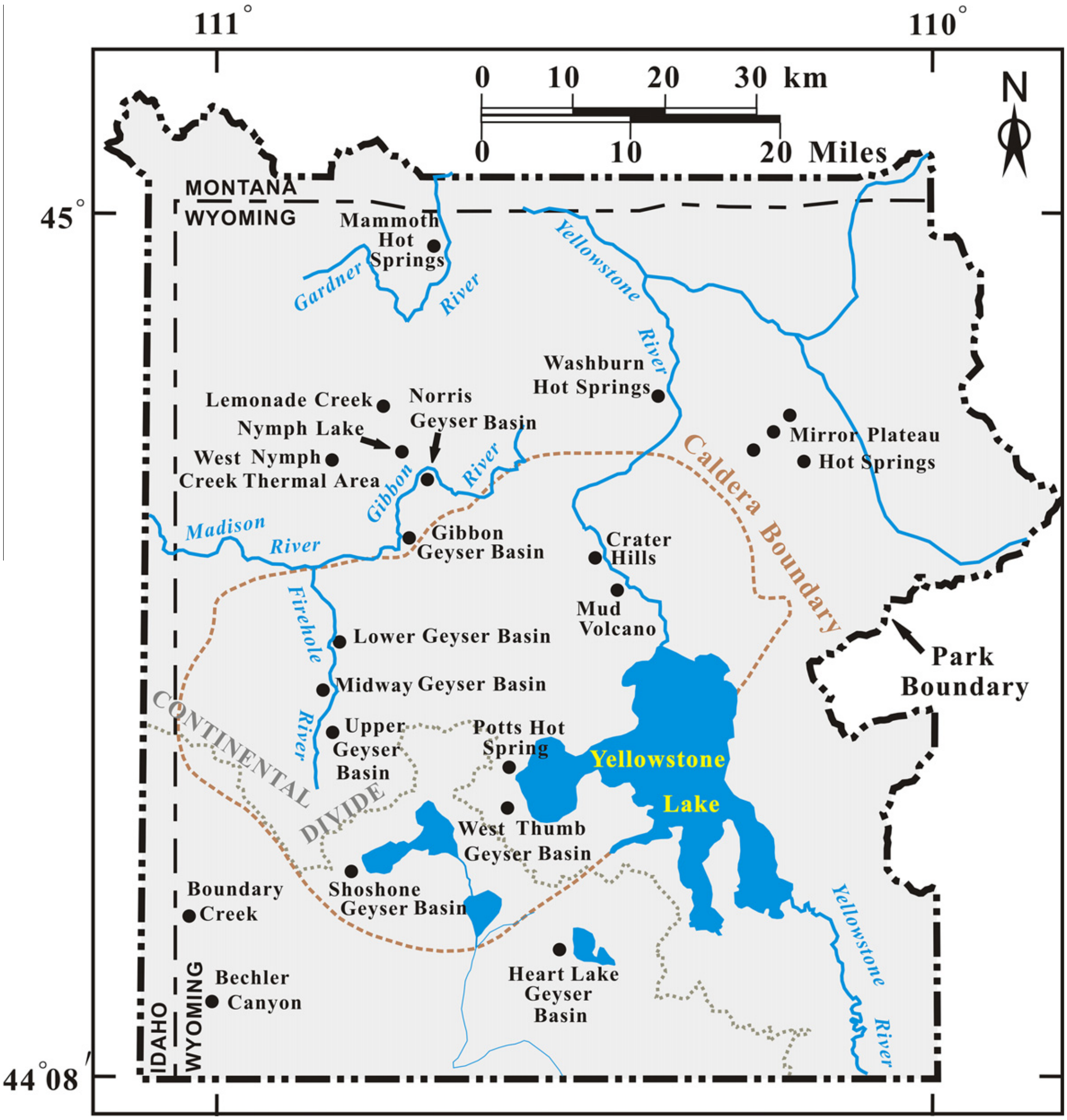

Fig. 1. Map of Yellowstone National Park showing the main areas of sample collection with solid circles. Most acid waters are found in or near Norris Geyser Basin, Mud Volcano, or Crater Hills.

aqueous speciation code (Ball and Nordstrom, 1991). The supporting analytical data for dissolved constituents (other than free fluoride-ion activity measurements) used in this study are found in Thompson and Hutchinson (1981), Thompson and Demonge (1996), Ball et al. (1998a,b, 2001, 2002, 2006, 2010), and McCleskey et al. (2005) data are given in Table 2.

2. MATERIALS AND METHODS

2.1. Sample locations

Yellowstone water samples were collected from thermal features at Mammoth Hot Springs, Norris Geyser Basin, Upper, Lower, and Midway Geyser Basin, Gibbon Geyser Basin, Potts Hot Spring Basin, Heart Lake Geyser Basin, Washburn Hot Springs, Crater Hills (includes Sulphur Spring), Mud Volcano (includes Sulphur Caldron), Shoshone Geyser Basin, Lemonade Creek, Nymph Lake, West Nymph Creek Thermal Area (WNCTA), Mirror Plateau Hot Springs, Bechler Canyon, and Boundary Creek (Fig. 1). The majority of acidic samples come from Norris Geyser Basin, Mud Volcano, or Crater Hills with a few samples from other basins. The samples were collected from springs arising from a variety of major rock types found in Yellowstone and a wide range of pH, temperature, chemical composition, and fluoride concentration.

2.2. Sample collection and field measurements

Water samples from springs, geysers, and large pools were collected with specialized equipment and filtered and preserved on site, the details of the processes and precautions were described by Nordstrom et al. (2009) and McCleskey et al. (2005). Samples for the determination of major cations and trace elements (As, Al, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, SiO_2, Sr, V, and Zn) were placed and stored in polyethylene bottles, which had been soaked in 5% HCl and rinsed three times with distilled water before collection. And then 1% (v/v) concentrated redistilled HNO_3 was added to stabilize the samples. The HNO_3 is high purity made by sub-boiling distillation and the HCl is high purity trace-metal free from GFS Co. Samples for major anions (Br, Cl, F, NO_3, and SO_4), alkalinity (HCO_3), and acidity were stored in polyethylene bottles with no chemical agents added. Container preparation and stabilization methods for samples analyzed for special redox species, stable isotopes, and organic carbon were summarized in Nordstrom et al. (2009). Water samples collected and documented from other reports used similar collection and preservation methods.

Measurements of electromotive force, used to calculate redox potential (Eh), pH, temperature, specific conductance, and H_2S were performed on-site. Measurements of Eh were checked against ZoBell's solution at the beginning of each day (Nordstrom, 1977). Measurements of Eh and pH were made on unfiltered sample water pumped from the source through an acrylic plastic flow-through cell, which minimized sample contact with air (Nordstrom et al., 2009). Field measurement of pH in thermal waters is challenging because of high-temperatures, complex sample matrices which are often supersaturated with CO_2, and surging water resulting from gas discharge. The details of measurement and calibrations can be found in Nordstrom et al. (2009). Lab measurements of temperature were very nearly 22 °C and the pH scale was based on the NBS conventions (Bates, 1973).

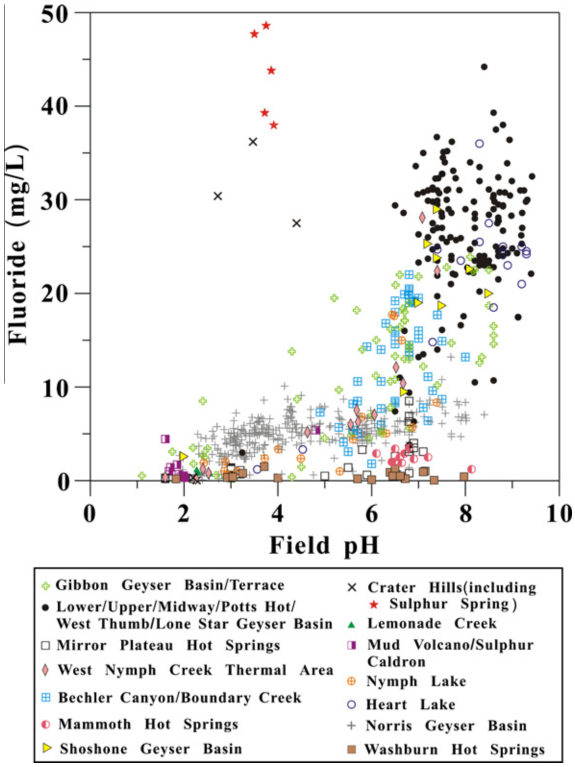

Fig. 2. Fluoride concentrations plotted with respect to pH values for Yellowstone hydrothermal waters (1975–2008). Data from Thompson and Hutchinson (1981), Thompson and Demonge (1996), Ball et al. (1998a,b, 2001, 2002, 2006), McCleskey et al. (2005), and Ball et al. (2010) data (see Supplementary material 1).

2.3. Analytical methods

2.3.1. *Major ions*

Major cations and most trace elements were determined by inductively coupled plasma-atomic emission spectrometry, major anions by ion chromatography except for alkalinity, which was determined by titration, and total and free fluoride, which were determined by ISE potentiometry. Most determinations had errors of about 5% or less and most detection limits were in the range of 1–100 ppb. Charge imbalances were commonly less than 5% and nearly all were less than 20% (Nordstrom et al., 2009). The analytical data were reported in Ball et al. (1998a, b, 2001, 2002, 2006, 2010) and McCleskey et al. (2005).

2.3.2. *Fluoride ISE method*

Both total dissolved fluoride and free fluoride were determined by ISE potentiometry. The fluoride ISE is highly sensitive, precise, and accurate for the measurement of fluoride-ion activity. The method for total dissolved fluoride uses a 10:1 mix of sample or standard with commercially available "total ionic strength adjustment buffer" (TISAB III) to eliminate aqueous complexes of fluoride,

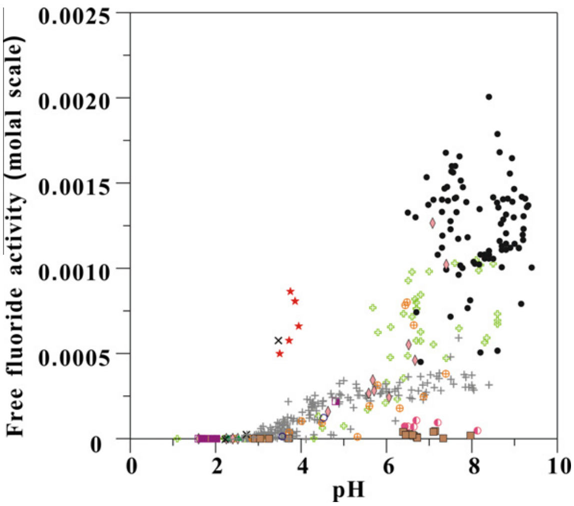

Fig. 3. Free-fluoride activity variation with pH for Yellowstone hydrothermal waters (1975–2008) calculated with WATEQ4F. Data from Thompson and Hutchinson (1981), Thompson and Demonge (1996), Ball et al. (1998a,b, 2001, 2002, 2006), McCleskey et al. (2005), and Ball et al. (2010, 2006) data (see Supplementary material 1). (Legends are the same as Fig. 2, but samples were not included for the calculation in which the Al concentration was missing).

buffer the pH, and keep the ionic strength constant. The TISAB III concentrate with CDTA (1, 2-diaminocyclohexane-*N*, *N*, *N*′, *N*′-tetraacetic acid, Orion 940911 reagent) was used. In addition, the reagent contains ammonium chloride, cresol red, and deionized water. Efforts have been made to evaluate the effect of matrix composition and some elements that could interfere with the fluoride determination with different methods (van den Hoop et al., 1996; McCleskey et al., 2004; Ball et al., 2006; Noh and Coetzee, 2006). High concentrations of aluminum in mine waters form strong complexes with fluoride, likely causing false results of low fluoride determination by ISE, which only measures free-fluoride ion (McCleskey et al., 2004). This interference can be eliminated by increasing the proportion of TISAB added to eliminate aqueous complexes of fluoride and ionic-strength effects (Midgley and Torrance, 1991).

Aqueous fluoride in Thompson and Hutchinson (1981), Thompson and Demonge (1996) was determined by ISE after 1:1 mixing with CDTA of lower concentration for decomplexing, 1 M NaCl for constant ionic strength adjustment, and acetate buffer to pH of 5.5 or after mixing with1 M NaCl, 0.058 M HCl, and 0.1 M tris-(hydroxymethyl) aminomethane. All of these reagents serve the same purpose.

The measurement of free F^- activity must be obtained without any added reagents, except to determine the effect of ionic strength on the standards by the addition of NaCl. The electrode was calibrated against a series of 5 or more KF standard solutions (Robinson et al., 1971) covering the linear working range of the electrode (about 100 ppb to at least 50 ppm). The activities of the standard solutions were calculated with the same code used for the speciation calculations, i.e. WATEQ4F (Ball and Nordstrom, 1991). The electrode was then used to measure the electromotive force of the sample solutions. Kinetic problems and nonlinearity of the electrode response begin to be noticeable below 100 ppb fluoride (or the equivalent activity, about 10^{-6} molar, for a mixed electrolyte solution) and the uncertainty increases substantially. To consider the ionic strength effect, 0.02 M, 0.05 M, and 0.1 M NaCl were added to the standard solutions sets to make the ionic strength of sample and standards comparable.

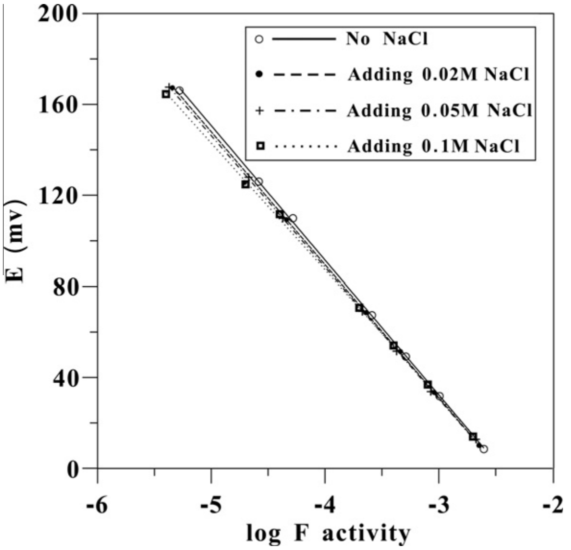

Fig. 4. The standard curves of free fluoride activity measurement by ISE method considering the effect of ionic strength by the addition of NaCl.

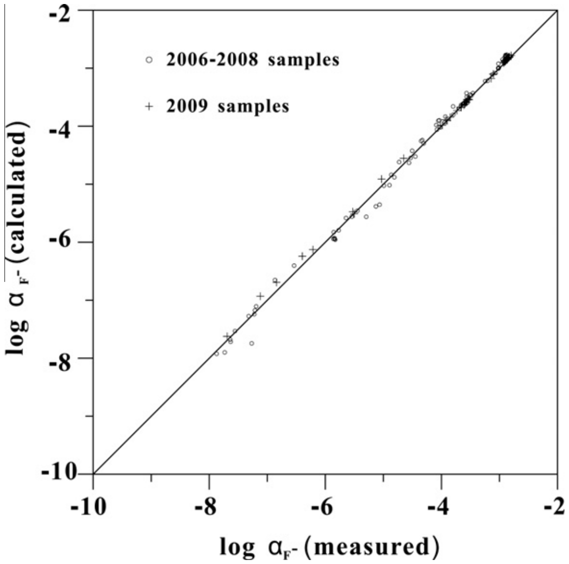

Fig. 5. Measured vs. calculated free fluoride ion activity distinguished by time of sample measurement. Data from 2006–2008 (Ball et al., 2010).

2.3.3. Speciation computations

For the speciation calculations, the pH and temperature of the sample needs to be the same as those for which the fluoride ion-activity measurements were made, i.e. ambient lab conditions. Results of the complete water analysis with ambient lab temperature (22 °C) and lab pH values were input data to the WATEQ4F speciation code (Ball and Nordstrom, 1991). Lab pH values can be found in Ball et al. (2001, 2002, 2006, 2010) and McCleskey et al. (2005). The main complexes of fluoride are given in Table 1 with the basic thermodynamic data (and references) used in WATEQ4F to calculate speciation. The PHREEQC code (Parkhurst and Appelo, 1999) was used for computations of speciation needed to prepare speciation diagrams. This code uses an ion-association aqueous model based on the original WATEQ code (Truesdell and Jones, 1974) and computes saturation indices, mass transfer, transport, equilibrium and irreversible reactions, kinetics, solution mixing, effects of temperature changes, and inverse modeling. The same database from WATEQ4F was used for the PHREEQC computations.

3. RESULTS AND DISCUSSION

3.1. Fluoride and water chemistry in Yellowstone

Hydrothermal water samples from Yellowstone National Park have a wide range of pH (1–10), temperature (25–95 °C), high concentrations of fluoride (up to 50 mg/

l), silica (up to 800 mg/l), arsenic (up to 15 mg/l), boron (up to 50 mg/l), and hydrogen sulfide (up to 8 mg/l) (Fig. 2 and Table 2) based on our data and those of Thompson and Hutchinson (1981) and Thompson and Demonge (1996). Numerous biotic and abiotic redox reactions, degassing processes, and mineral-precipitation occur in this hydrothermal system (Nordstrom et al., 2005).

Fig. 2 shows that the total aqueous fluoride concentration for most of major thermal areas in Yellowstone varies with pH. Generally, the occurrence of high fluoride concentrations is restricted to waters with field pH values higher than 6 and temperatures higher than 50 °C. These conditions are found in Lower, Midway, Upper and West Thumb Geyser Basins, and parts of Bechler Canyon and Boundary Creek. An exception is in Crater Hills where 7 samples in or near Sulphur Spring have high fluoride concentrations and low pH values. These samples are also unusually enriched in boron (23.5–28.5 mg/l), arsenic (3.79–5.89 mg/l), silica (694–743 mg/l) and lithium (5.67–7.78 mg/l). In Mammoth Hot Springs area, the total dissolved fluoride concentration of the water samples are typically less than 5 mg/l with pH ranging from 6 to 8. Water samples with pH less than 6 commonly contained less than 10 mg/L of fluoride and were generally found in Norris Geyser Basin. High concentrations of fluoride were generally associated with temperatures greater than 50 °C.

For thermal waters in YNP, both fluoride concentration and free-fluoride activity are pH dependent. Calculated free-fluoride activity is lower in acidic water and higher in alkaline water. The fluoride activity is nearly zero when pH is less than 3. As pH increases from 6 to 8, fluoride activity increases sharply (Fig. 3) and some of the outliers in Fig. 2 (Crater Hills samples) are now more in line with the general trend.

3.2. Comparison of measured vs. calculated free fluoride ion activity

The effect of ionic strength on the standard solutions was considered by adding increasing amounts of NaCl (Fig. 4) and recomputing the activity of free fluoride with WATEQ4F. Free-fluoride activities were determined from the appropriate standard curve which had comparable ionic strength to the water samples. With an increase in ionic strength, the slope of the standard curve decreases.

The results of the comparison between free-fluoride activities measured by ISE and those calculated with WATEQ4F are summarized in Fig. 5. It should be pointed out that the free-fluoride activity in water samples collected in 2006–2008 were measured in 2008, while the samples in 2009 were measured 2 weeks after collection. The values of free-fluoride activity cover a broad range of about 5 orders of magnitude. The results of the comparison are generally good, for such a wide range of pH and composition.

A deviation plot is a more sensitive measure of the variance. The deviations in percent difference vs. measured values of free-fluoride activity are shown in Fig. 6. The agreement varies by 0.3–30% in more than 90% of the 2006–2008 samples with free-fluoride activity at or above 10^{-6} molar. The deviation becomes greater than 50% when

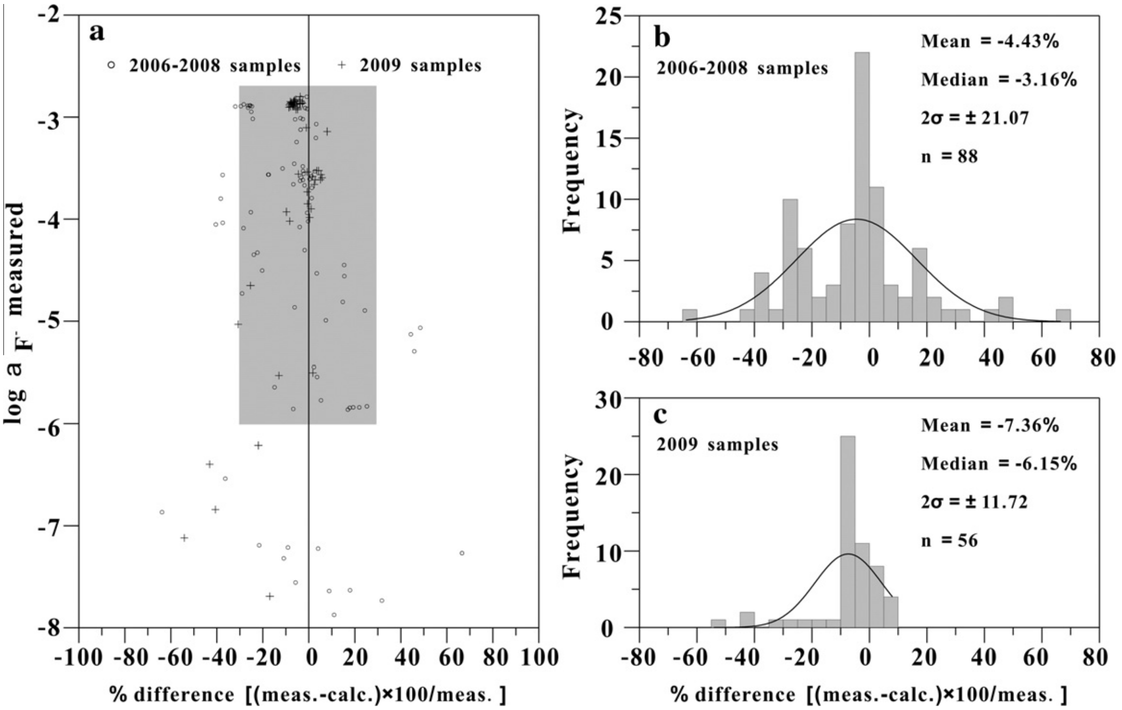

Fig. 6. The deviation between measured values of free-fluoride activity and WATEQ4F-calculated results in percent difference. (a) Percent of difference relative to measured free-fluoride acitivity, (b) frequency plot for % difference for 2006–2008 samples (Ball et al., 2010) and (c) frequency plot for % difference for 2009 samples (Supplementary material 1; The grey box shows that more than 90% of the samples fit within ±30% when the free fluoride activity at or above 10^{-6} molar).

Table 3

Temperature, pH, Cl concentration, fluoride concentration, measured free-fluoride activity (molal scale), and calculated free-fluoride activity (molal scale) for 2009 samples. Basin designations are NGB = Norris Geyser Basin, CH = Crater Hills, WNCTA = West Nymph Creek Thermal Area, FR = Firehole River, LGB = Lower Geyser Basin.

Sample ID	Location	Basin	Temperature (°C)	pH	Cl (mg/L)	F (mg/L)	Free F activity (measured)**	Free F activity (calculated)**
09WA102	Lifeboat Spring***	NGB	51.0	3.67	627	5.47	1.11×10^{-4}	1.39×10^{-4}
09WA103	Persnickety Geyser***	NGB	82.1	5.14	630	5.80	2.44×10^{-4}	2.38×10^{-4}
09WA105	Cojones I***	NGB	76.8	2.48	540	4.44	3.14×10^{-6}	3.16×10^{-6}
09WA106	Cojones II***	NGB	67.2*	3.61	678	6.28	9.42×10^{-5}	1.11×10^{-4}
09WA107	Unnamed	NGB	89.2	6.57	547	6.27	3.10×10^{-4}	2.89×10^{-4}
09WA108	Cinder Pool	NGB	90.6	4.23	643	6.56	1.85×10^{-4}	1.94×10^{-4}
09WA109	Bathtub Spring	NGB	89.7	4.18	512	6.01	1.26×10^{-4}	1.28×10^{-4}
09WA110	Emerald Spring	NGB	83.8	4.31	596	6.64	2.62×10^{-4}	2.69×10^{-4}
09WA111	Minute Geyser	NGB	92.3	7.26	592	6.24	2.99×10^{-4}	2.80×10^{-4}
09WA112	Branch Spring	NGB	78.5	4.18	404	4.05	1.39×10^{-4}	1.47×10^{-4}
09WA113	Second Eruptor***	NGB	91.2	8.03	665	6.34	2.99×10^{-4}	2.89×10^{-4}
09WA114	Unnamed	NGB	83.4	4.10	282	3.23	1.44×10^{-7}	2.11×10^{-7}
09WA115	Unnamed	NGB	68.0	4.10	90.4	0.63	7.59×10^{-8}	1.19×10^{-7}
09WA116	Unnamed	NGB	72.9	2.33	248	2.78	6.12×10^{-7}	7.46×10^{-7}
09WA117	Nymph Lake	NGB	89.6	3.70	114	3.30	2.96×10^{-6}	3.51×10^{-6}
09WA118	Unnamed	NGB	82.4	2.33	212	3.63	4.01×10^{-7}	5.69×10^{-7}
09WA119	Unnamed	CH	81.2	2.21	2.0	0.64	3.26×10^{-8}	6.67×10^{-8}
09WA120	Sulphur Spring	CH	88.2	3.93	1001	37.9	7.21×10^{-4}	8.77×10^{-4}
09WA121	Unnamed	CH	86.1	2.21	1.6	0.26	2.04×10^{-8}	2.58×10^{-8}
09WA122	Cistern Spring	NGB	83.1	4.80	536	5.64	2.55×10^{-4}	2.47×10^{-4}
09WA123	Unnamed	WNCTA	61.9	5.57	9.9	5.93	2.90×10^{-4}	2.70×10^{-4}
09WA124	Steamboat Geyser	NGB	82.0	6.27	571	5.77	2.72×10^{-4}	2.47×10^{-4}
09WA125	Green Dragon Spring	NGB	90.2	2.87	488	5.40	9.22×10^{-6}	1.36×10^{-5}
09WA126	Unnamed	NGB	77.6	2.72	503	5.71	1.97×10^{-5}	2.80×10^{-5}
09WA128	Chocolate Pots I	CP	52.2	5.96	32.2	4.48	2.19×10^{-4}	2.00×10^{-4}
09WA129	Chocolate Pots II	CP	62.0	6.24	33.4	4.96	2.43×10^{-4}	2.26×10^{-4}
09WA131	Lonestar Geyser	FR	36.7*	9.14	534	17.4	7.87×10^{-4}	7.95×10^{-4}
09WA132	Quagmire Group Spring	LGB	89.3	8.72	318	27.7	1.23×10^{-3}	1.29×10^{-3}
09WA138	Ojo Caliente	LGB	93.5	7.52	330	32.7	1.41×10^{-3}	1.57×10^{-3}

* Flow cell temperature.

** At 22 °C 594.

*** Unofficial name.

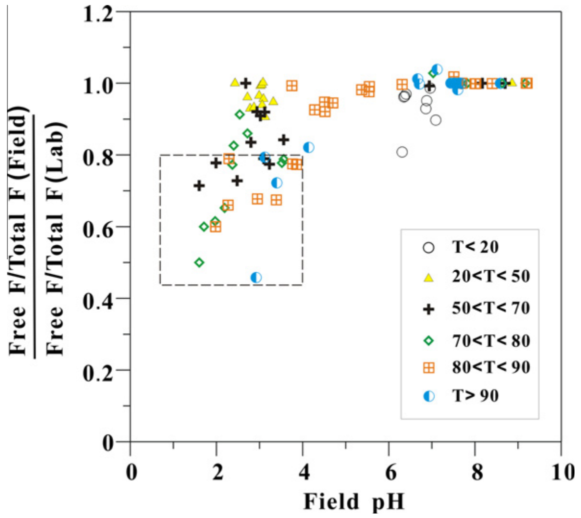

Fig. 7. Change of free- to total-fluoride concentration ratio with field pH under field (field pH and temperature) and lab conditions (lab pH and 22 °C).

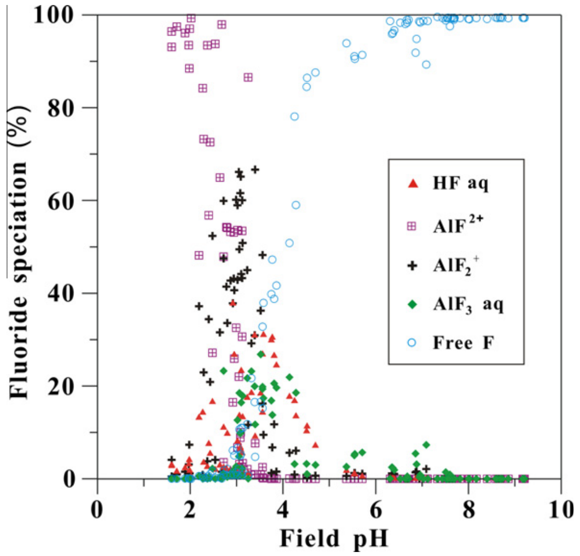

Fig. 9. Fluoride speciation vs. pH in hydrothermal water samples calculated by WATEQ4F.

the fluoride activity is below 10^{-6} molar. This increased variance is related to the non-Nernstian response of the ISE as it approaches the detection limit and to differences in ionic strength and solution composition between samples and standards.

The deviation between fluoride activities obtained by the two methods for the 2009 samples was much less (0.3–10% for 95% of samples with free-fluoride activity greater than 10^{-6} molar; Table 3) than the 2006–2008 data. It provides excellent corroboration for chemical speciation models.

Laboratory pH measurements are made typically near 22 °C which can be as much as 70 °C lower than the temperature at which the sample pH was measured in the field and this difference will affect fluoride activities. To evaluate these effects the calculated results under field conditions (field pH and field temperature) were compared with those under lab conditions (lab pH and 22 °C; Fig. 7). Results show that the difference is associated mostly with samples that have lower field pH (<4) and higher temperature (>50 °C).

In Fig. 7, the data in the dashed square that have bigger differences of free- to total-fluoride concentration ratio between results under field and lab conditions mostly have lower concentrations of fluoride (0.5–5.5 mg/l), higher aluminum concentrations, and lower free- to total-fluoride ratio (0.1–50%). Free-fluoride activity is sensitive to the variation of pH at the range of 1–4. The free- to total-fluoride ratio becomes relatively constant at pH > 6. Furthermore, differences in pH values between field and lab measurements are the results of Fe oxidation and

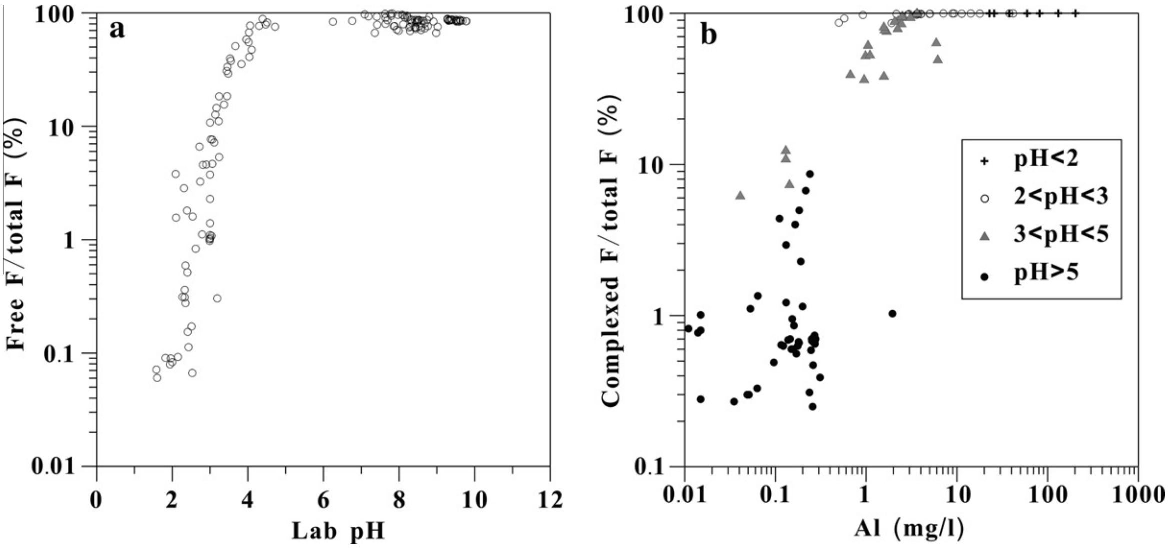

Fig. 8. Free- to total-fluoride ratio and complexed F to total fluoride ratio affected by (a) lab pH and (b) Al concentration, respectively.

hydrolysis, the oxidation of reduced S species, CO_2 degassing, and the change in temperature (Nordstrom et al., 2009). The differences are greatest at field pH < 3 and higher temperature (Ball et al., 2006).

3.3. Fluoride speciation in hydrothermal waters under various pH conditions

The free- to total-fluoride concentration ratio varied as a function of pH, ranging from <1% free fluoride at low pH values to >99% free fluoride at high pH. The ratio is greater than 90% with pH values >6 (Fig. 8a), because elevated concentrations of OH^- ions will outcompete F^- in complexes with cations. Only 10% of the fluoride occurred as free-fluoride ion when pH is less than 4 because of the formation of $HF^0_{(aq)}$ and aqueous complexation with aluminum. Similar trends in speciation for fluoride were described by Kraynov et al. (2004) for non-thermal groundwaters. At lower pH, some fluoride might be partially lost from volatilization of HF gas. Acid waters at Yellowstone consist mostly of sulfuric acid. When this water makes contact with a mineral like fluorite then HF gas is produced which will separate into the volatile steam phase (Ellis and Mahon, 1977).

A positive correlation was observed between aluminum concentration and complexed-F concentration which is equal to the difference between the free- and the total-fluoride concentration (Fig. 8b). Complexing can often be the single most important factor determining the total concentration of dissolved fluoride. Complexes with fluoride (AlF^{2+}, AlF_2^+, AlF_3^0, AlF_4^-, AlF_5^{2-} and AlF_6^{3-}) are stable and significantly influence the solubility of aluminum compounds. Matin (1996) stated that the presence of fluoride will reduce the toxicity of Al^{3+} in relation to plants, fish, and human. Numerous studies have been done previously because of concern about the potential toxic effects of aluminum-fluoride complexes (Matin, 1996; Stevens et al., 1997; Frankowski et al., 2010) and on their rate of formation (Plankey et al., 1986).

Aqueous fluoride speciation is mainly controlled by pH and the concentrations of other components that can form complexes with fluoride. In addition to Al, fluoride may be associated with other metal ions to form complexes: $NaF_{(aq)}$, $CaF^+_{(aq)}$, $MgF^+_{(aq)}$, and FeF_n^{3-n} (aq) ($n = 1, 2, 3$). Another component which complexes with $F^-_{(aq)}$ is boric acid, forming $BF_n(OH)^-_{4-n(aq)}$ which need to be considered, because the boron content of thermal waters can be high.

Fluoride species distribution were calculated with WATEQ4F code using the data of 106 hydrothermal waters samples collected from YNP in 2006–2008 (Ball et al., 2010). The results show that free fluoride and major complexes ($HF^0_{(aq)}$, AlF^{2+}, AlF_2^+ and AlF_3^0) account for more than 95% of total fluoride. In a few samples complexes species of AlF_4^-, FeF^{2+}, FeF_2^+, MgF^+ and $BF_2(OH)_2^-$ comprised 1–10% of the total dissolved fluoride (Table 2). For example, $BF_2(OH)_2^-$ species generally accounted for less than 0.1% of total fluoride. But it increased up to 1.76% in acidic Sulphur Spring, which contains abnormally high concentrations of boron (23.5 mg/l). The SiF_6^{2-} species only appears in Sulphur Spring with extremely high concentrations of SiO_2 (743 mg/l).

3.4. Controlling factors on aqueous fluoride species distribution from speciation simulations

Free F^-, H–F complexes, and Al–F complexes are the main fluoride species in hydrothermal waters. These species are shown as a function of pH for 2006–2008 samples in Fig. 9 using field pH and temperature and output from the WATEQ4F code. This figure allows us to visualize the change in predominant fluoride species with pH. Under the most acidic conditions the AlF^{2+} complex predominates and under the most basic conditions, free fluoride predominates. The range is from <1% free fluoride at low pH values (pH < 3) to >95% free fluoride at high pH (pH > 7). The proportion of AlF^{2+} decreased from 99% to <1% when pH increased from 2 to 4. At a pH near 3, AlF_2^+ predominates peaking at 66% of the speciation, and at a pH near 3.5 AlF_3^0 begins to increase just before free-fluoride ion becomes predominate for pH > 3.5. The species $HF^0_{(aq)}$ also competes with the AlF_2^+ and AlF_3^0 species in the pH range of 3–4. The activity of free fluoride continues to predominate from pH > 3.5 but makes a small jump from about 92% of the speciation to effectively 100% of the speciation above a pH of 7. This jump is caused by some persistence of aluminum-fluoride complexes up to this pH value.

This complex display of speciation can be interpreted with the aid of speciation simulations using the PHREEQC code (Parkhurst and Appelo, 1999). In the absence of Al, $HF^0_{(aq)}$ is the predominant species in water at lower pH (<3) with a small proportion of HF_2^-. Free fluoride accounts for 90% when the pH is greater than 5 (Fig. 10). Generally, in the absence of aluminum in acid solution with pH < 3, fluoride occurs predominantly as weakly dissociating hydrofluoric acid $HF^0_{(aq)}$ (Bebeshko, 2004; Ozsvath,

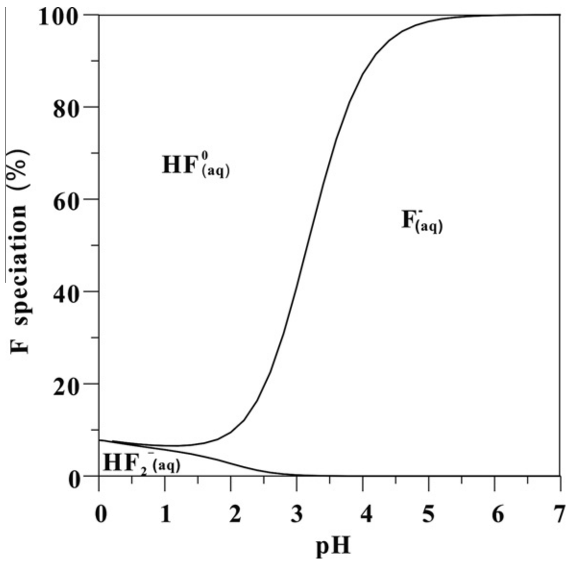

Fig. 10. Fluoride speciation in water varies with pH in the absence of Al. These speciation boundaries were calculated with the PHREEQC code and the WATEQ4F database.

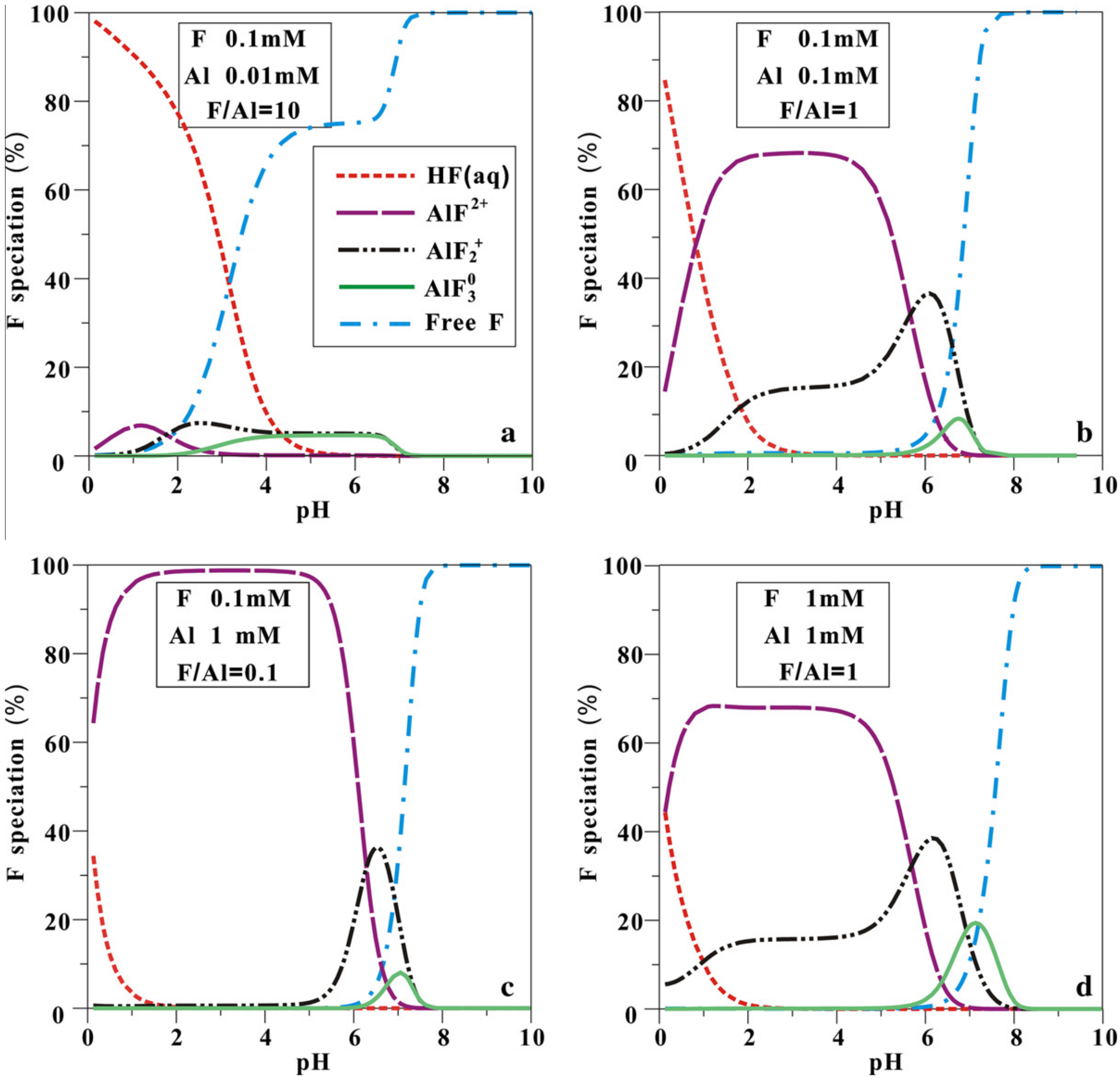

Fig. 11. Fluoride aqueous speciation varies with pH and F, Al concentration simulated by PHREEQC.

2009, Fig. 10). However, high concentrations of aluminum (up to 12 mM) occurred in most YNP hydrothermal waters with pH less than 3.

When Al is considered, the speciation of fluoride becomes more complicated. Based on our modeling results, the main fluoride species (free F, HF, and Al–F complexes) are controlled not only by pH but also by the ratio of F and Al concentrations. The fluoride aqueous speciation variation was simulated using 0.1 and 1 mM concentrations of F and 0.01, 0.1, and 1 mM concentrations of Al and ratios of 10, 1 and 0.1 (Fig. 11a–d).

When Al is included but less than 0.1 mM, $HF^0_{(aq)}$ is the predominant species in the range of pH 0–3. As the Al concentration increases above 0.1 mM, the AlF^{2+} species predominates up to a pH of 6 where free-fluoride ion predominates. In Fig. 11a the small step increase in free fluoride at a pH of 7 is observed just as in Fig. 10 and it is related to the continued stability of a few percent of the AlF_2^+ and AlF_3^0 species up to pH 7. As the Al concentrations increases at constant F concentration (Fig. 11a–c), the species AlF_2^+ becomes a more prominent proportion but limited to a narrow pH window close to 6. With an increase in both Al and F concentrations (Fig. 11d), the AlF_3^o species increases in importance briefly at pH 7. These simulations help to decipher the fluoride species distribution found in field samples but some differences will occur because the simulations were done at 25 °C whereas the water samples were at higher temperatures and there may be some ionic strength effects.

4. CONCLUSIONS

Hydrothermal water samples from Yellowstone National Park (YNP) have a wide range of pH (1–10), temperature, and high concentrations of fluoride (up to 50 mg/l). High fluoride concentrations are found consistently in waters with field pH higher than 6 and temperature higher than 50 °C.

More than 140 water samples from YNP collected in 2006–2009 have been analyzed for free-fluoride activity by ion-selective electrode (ISE) method. Agreement between analytical and calculated aqueous free-fluoride activities was within 0.3–30% for more than 90% samples at or above 10^{-6} molar, indicating a generally high reliability of the calculated speciation for fluoride by the WATEQ4F code. The deviation becomes greater than 50% when the fluoride activity is below 10^{-6} molar, which could be related either to slow rates of equilibration for fluoride ISE at low activities or the effect of ionic strength and compositional differences between samples and standards.

The range of the free- to total-fluoride concentration ratio was from <1% at low pH values to >99% at high pH. Such a wide range could be explained by strong complexing with H^+ and Al^{3+} under acidic conditions. Speciation calculation results show that free fluoride and major complexes (HF, AlF_2^+, AlF^{2+} and AlF_2^0) account for more than 95% of total fluoride in YNP hydrothermal waters. Occasionally, some complexes species like AlF_4^-, FeF^{2+}, FeF_2^+, MgF^+ and $BF_2(OH)_2^-$ may comprise 1–10% when the concentrations of Fe, Mg or B were high. The ratio of main fluoride species (free F, HF, and Al–F complexes) to total fluoride varies as a function of pH, also controlled by F/Al ratio and F, Al concentration.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2011.05.028.

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