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Mineral saturation states in natural waters and their sensitivity to thermodynamic and analytic errors. *Etat de saturation des minéraux dans les eaux naturelles et sensibilité des tests aux données thermodynamiques et aux erreurs analytiques*

Darell.Kirk Nordstrom, James W. Ball

Résumé
Les indices de saturation calculés sur ordinateur avec le programme WATEQ4F à partir d'analyses chimiques d'une solution de socle granitique et d'eaux de surface influencées par des exhaures minières acides sont fréquemment saturés ou sursaturés par rapport à la calcite, la fluorine, la barytine, la gibbsite et la ferrihydrite. Les eaux profondes du socle granitique de Stripa (Suède) sont sursaturées par rapport à la calcite et la fluorine. Les eaux acides des mines du bassin versant du Leviathan (Californie) sont sursaturées par rapport à la barytine d'un facteur voisin de trois. Les eaux de mines sont également sursaturées d'un facteur 10 par rapport à la forme la plus soluble de l'hydroxyde ferrique, mais voisines de la saturation par rapport à la gibbsite microcristalline. Une analyse de sensibilité des tests a été réalisée en faisant varier les paramètres analytiques et thermodynamiques auxquels les indices de saturation sont les plus sensibles. Pour la calcite, la fluorine et la barytine l'état de sursaturation paraît le plus réaliste car il n'est que très peu lié aux sources d'incertitudes. La sursaturation apparente par rapport à la gibbsite semble très probablement liée, par le degré de cristallinité, aux incertitudes sur la solubilité. La sursaturation apparente par rapport à l'hydroxyde ferrique est probablement due aux particules colloïdales de faible taille (< 0, 1 µm) qui ne peuvent pas être séparées des échantillons d'eau par filtration classique sur le terrain. D'autres explications possibles ne peuvent pas être abordées facilement.

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MINERAL SATURATION STATES IN NATURAL WATERS AND THEIR SENSITIVITY TO THERMODYNAMIC AND ANALYTIC ERRORS

Darrell Kirk NORDSTROM* and James W. BALL*

ABSTRACT — Saturation indices computed with WATEQ4F for chemical analyses from a groundwater in crystalline bedrock and a surface water receiving acid mine drainage are frequently at or above saturation with respect to calcite, fluorite, barite, gibbsite and ferrihydrite. Deep granitic groundwaters from Stripa, Sweden, are supersaturated with respect to calcite and fluorite. Acid mine waters from the Leviathan Mine drainage basin in California are supersaturated with respect to barite by about a factor of three. These mine waters also are 10 times supersaturated with respect to the most soluble form of ferric hydroxide but are near saturation with respect to microcrystalline gibbsite. A sensitivity analysis has been peformed by varying the analytic and thermodynamic parameters for which the saturation indices are most sensitive. For calcite, fluorite and barite, the supersaturation effect appears to be real because it is only slightly decreased by sources of uncertainty. Apparent supersaturation for gibbsite is most likely caused by the degree of crystallinity on solubility behavior. Apparent supersaturation for ferric hydroxide is likely caused by small colloidal particles ($< 0.1\ \mu m$) in the water sample that cannot be removed by standard field filtration, although several other possible explanations cannot be easily excluded.

Mineral saturation, Sensitivity analysis, Calcite, Fluorite, Barite, Gibbsite, Ferrihydrite, Speciation, Saturation indices

Etat de saturation des minéraux dans les eaux naturelles et sensibilité des tests aux données thermodynamiques et aux erreurs analytiques

RÉSUMÉ — Les indices de saturation calculés sur ordinateur avec le programme WATEQ4F à partir d'analyses chimiques d'une solution de socle granitique et d'eaux de surface influencées par des exhaures minières acides sont fréquemment saturés ou sursaturés par rapport à la calcite, la fluorine, la barytine, la gibbsite et la ferrihydrite. Les eaux profondes du socle granitique de Stripa (Suède) sont sursaturées par rapport à la calcite et la fluorine. Les eaux acides des mines du bassin versant du Leviathan (Californie) sont sursaturées par rapport à la barytine d'un facteur voisin de trois. Les eaux de mines sont également sursaturées d'un facteur 10 par rapport à la forme la plus soluble de l'hydroxyde ferrique, mais voisines de la saturation par rapport à la gibbsite microcristalline. Une analyse de sensibilité des tests a été réalisée en faisant varier les paramètres analytiques et thermodynamiques auxquels les indices de saturation sont les plus sensibles. Pour la calcite, la fluorine et la barytine l'état de sursaturation paraît le plus réaliste car il n'est que très peu lié aux sources d'incertitudes. La sursaturation apparente par rapport à la gibbsite semble très probablement liée, par le degré de cristallinité, aux incertitudes sur la solubilité. La sursaturation apparente par rapport à l'hydroxyde ferrique est probablement due aux particules colloïdales de faible taille ($< 0{,}1\ \mu m$) qui ne peuvent pas être séparées des échantillons d'eau par filtration classique sur le terrain. D'autres explications possibles ne peuvent pas être abordées facilement.

Saturation des minéraux, Analyse de sensibilité, Calcite, Fluorine, Barytine, Gibbsite, Ferrihydrite,
Spéciation, Indices de saturation

INTRODUCTION

Speciation computations often are made for water analyses to test their degree of saturation with respect to the solubilities of various minerals, based on principles of chemical equilibrium. These computations provide information on the tendency of the water to dissolve or precipitate minerals and, when combined with hydrologic and mineralogic data, are an essential tool in the hydrogeochemical interpretation of an aquatic system (DREVER, 1988 ; NORDSTROM and MUNOZ, 1986). Unfortunately, the reliability of the computations rarely is examined with regard to propagation of errors.

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* U.S. Geological Survey, MS-420, 345 Middlefield Road, Menlo Park, California 94025, USA.

The saturation state of a natural water with respect to a mineral phase is defined as the log of the ratio of the ion activity product (IAP) to the solubility product constant (Ksp), or the saturation index (S.I.) :

$$\text{S.I.} = \log(\frac{\text{IAP}}{\text{Ksp}})$$

If the S.I. is zero the water composition reflects solubility equilibrium, a negative value suggests undersaturation, or the tendency to dissolve a mineral, and a positive value suggests supersaturation, or the tendency to precipitate a mineral.

Two noteworthy papers by SCHECHER and DRISCOLL (1987, 1988) evaluate both the thermodynamic and analytic uncertainties that can affect calculations of aluminum speciation in dilute, acidic stream-waters. They found that the largest source of uncertainty was the Ksp for gibbsite used in the calculation of its saturation index. However, they did not separate the degree-of-crystallinity problem for gibbsite in the sense of only considering the error for « microcrystalline » gibbsite solubility (HEM and ROBERSON, 1967) or for « natural » gibbsite solubility (MAY *et al.*, 1979), but rather the whole range of solubilities from many investigations was used as the uncertainty. They also found the range of published equilibrium constants for aluminum hydrolysis and ion-pairing reactions resulted in significantly larger uncertainties than those errors reported from any one individual experiment. This conclusion is to be expected since the standard deviation of all literature values for a reaction (which approximates the accuracy or at least the consistency of data) will always be larger than the standard deviation from one set of data in a single investigation (which measures the precision). They found that, for dilute waters from the Adirondacks, the uncertainties in aluminum, fluoride and pH determinations were most critical for the sampling and analytical errors, although these uncertainties (as determined by triplicate analyses) were no worse than the uncertainties for equilibrium constants.

Errors in speciation computations are propagated from three sources : (1) uncertainties in the thermodynamic database, (2) uncertainties in analytical data and (3) uncertainties in the equilibrium assumption. In this paper we shall consider all three sources of uncertainty for analyses of waters from two field sites. Errors propagated from selected major analytical and thermodynamic components are examined for their effects on the saturation indices of gibbsite, ferrihydrite, barite, calcite and fluorite.

I — PROCEDURE

1. Sources of analytical data

a) Stripa groundwater data

More than 50 analyses, of groundwaters collected from the surface to over 1 km depth in a granite in central Sweden, were obtained as part of the International Stripa Project (NORDSTROM *et al.*, 1989). Concentrations of all major constituents were determined, unstable parameters were measured on site, and inter-laboratory comparisons have assured quality control. Several trace constituents also were determined. These groundwaters are basic (pH = 8.5 to 10.0) Na-Ca-Cl type at depths greater than 500 m and reflect water-rock interactions with minerals known to occur in the granitic bedrock. Total dissolved solids reach a maximum of 1250 mg/L but are known to be highly variable from one water-bearing fracture zone to the next.

b) Leviathan stream-water data

About 60 complete analyses for major and trace elements were obtained for stream-waters containing varying amounts of acid drainage from the Leviathan mine, located in eastern California, a few kilometers south of Lake Tahoe. The pH ranges from 1.8 to 8.8 and metals such as dissolved iron range from more than 1 g/L to 1 μg/L or less. These analyses have undergone considerable scrutiny for accuracy and precision, by comparing the results from direct-current plasma, inductively-coupled plasma, flame and flameless atomic absorption and UV-visible spectrometric determinations.

2. Computational procedure

All water analyses were speciated using the computer program WATEQ4F (BALL *et al.*, 1987) and the output was transferred to a plot file with EQPRPLOT (unpublished program) and plotted with PROPLOT (Cogent Software)[*]. Since all of these waters are of low ionic strength, the Truesdell-Jones parameters (used with the WATEQ series of programs) are of sufficient accuracy for activity coefficient corrections. Solubility product constants for the five minerals examined in this study are shown in table I. Equilibrium constants for ion-pairing reactions can be found in previous publications on the WATEQ programs (see BALL *et al.*, 1987).

Table I

Solubility product constants for minerals

Produits de solubilité des minéraux

Mineral	Formula	logKsp(298.15 K)	Reference
Calcite	$CaCO_3$	-8.48 ± 0.02	Plummer and Busenberg (1982)
Fluorite	CaF_2	-10.96 ± 0.10	Nordstrom and Jenne (1977)
Fluorite	CaF_2	-10.58 ± 0.17	Brown and Roberson (1977)
Barite	$BaSO_4$	-9.98 ± 0.02	Ball, et al. (1980)
Gibbsite			
crystalline	$Al(OH)_3$	8.11 ± 0.02	May, et al. (1979)
microcrystalline	$Al(OH)_3$	9.35 ± 0.30	Hem and Roberson (1967)
amorphous	$Al(OH)_3$	10.8	Feitknecht and Schindler (1963)
Ferrihydrite	$Fe(OH)_3$	5.0	Langmuir and Whittemore (1971)

Ion-activity products and S.I. values cover a wide range in the original data set for these waters and do not lend themselves to statistical summaries without pre-selection of values based on knowledge of geochemical processes at each site. Therefore, the fifty or more samples from each site that are presented in this paper were selected from a larger set based on trends and processes explained below.

3. Representation of the data

The original data set of over 100 water analyses from the Stripa site, when speciated to give S.I. values for calcite and fluorite, produced many undersaturated values for shallow subsurface groundwaters. These values were eliminated from this investigation for several reasons : (1) it was important to know whether the supersaturated values were real or within the analytical and thermodynamic uncertainties, (2) the undersaturated values are in the zone of active groundwater circulation and active dissolution of calcite and fluorite, and (3) the supersaturated values, as a group, more closely approximate a normal error distribution whereas inclusion of the undersaturated values would significantly skew the distribution. For these reasons only those analyses from the Stripa data set that gave S.I. values for calcite and fluorite at or above saturation were selected.

Similarly, the Leviathan stream-waters show a considerable range of S.I. values for $Fe(OH)_3$ (« ferrihydrite »), $Al(OH)_3$ (« gibbsite ») and $BaSO_4$ (« barite ») from undersaturation to supersaturation.

Undersaturation for ferrihydrite and microcrystalline goethite occurs in the more acidic waters ($pH < 3.5$) because dissolved iron is primarily Fe(II) as a result of pyrite oxidation and slow oxidation kinetics at these low pH values. These were not included. The remaining S.I. values are distributed over a ± 1.5 unit range around the ferrihydrite log Ksp. Gibbsite undersaturation occurs because there is insufficient aluminum hydrolysis below

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[*] The use of trade, brand, or product names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

pH = 4.5. The S.I. values range almost 2 orders of magnitude on either side of the saturation line for pH > 4.0. It is difficult to say exactly where undersaturation occurs except that a natural break in this data set occurs at a pH = 4.5 because above this value the S.I. results all correlate with the $Al(OH)_3$ stoichiometry (NORDSTROM and BALL, 1986 ; see fig. 1). Barite undersaturation is less common and usually occurs in downstream locations, as a result of dilution. Undersaturated analyses were eliminated from the sensitivity computations which were not consistent with the appropriate mineral stoichiometry.

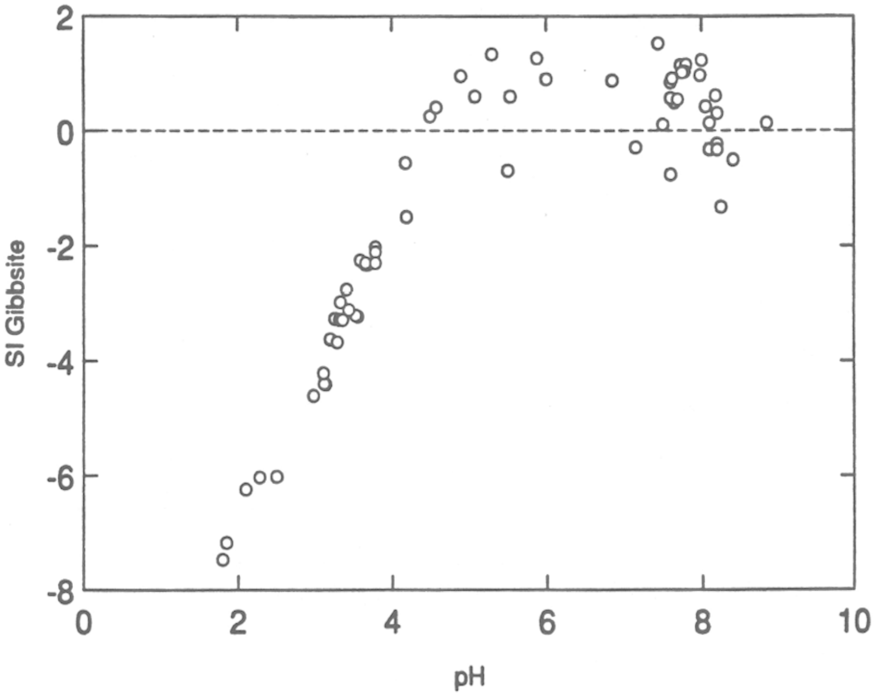


Fig. 1 — S.I. gibbsite plotted with respect to pH for Leviathan data.
Indices de saturation (S.I.) de la gibbsite en fonction du pH pour les données de Leviathan.

As a test for normal distributions the mean, median and skewness were calculated for each group. The skewness was determined from the formula :

$$Sk = \frac{3(\text{mean-median})}{\text{s.d.}}$$

where Sk is the skewness, and s.d. is the standard deviation. The mean, median and skewness for each group are shown in table II. The data are plotted in the form of histograms showing the frequency as a function of the S.I. value (fig. 2-7).

Table II
Means, medians and skewness of S.I. values
Moyennes, médianes et asymétries des valeurs d'indices de saturation S.I.

	n	Mean	Median	Skewness	Std. Dev.
Calcite	66	0.429	0.449	-0.188	0.313
Fluorite	45	0.651	0.668	-0.134	0.388
Barite	57	0.154	0.314	-0.7924	0.606
Gibbsite	40	9.66	10.04	-1.210	0.946
Ferrihydrite	58	0.312	0.298	0.0468	0.895

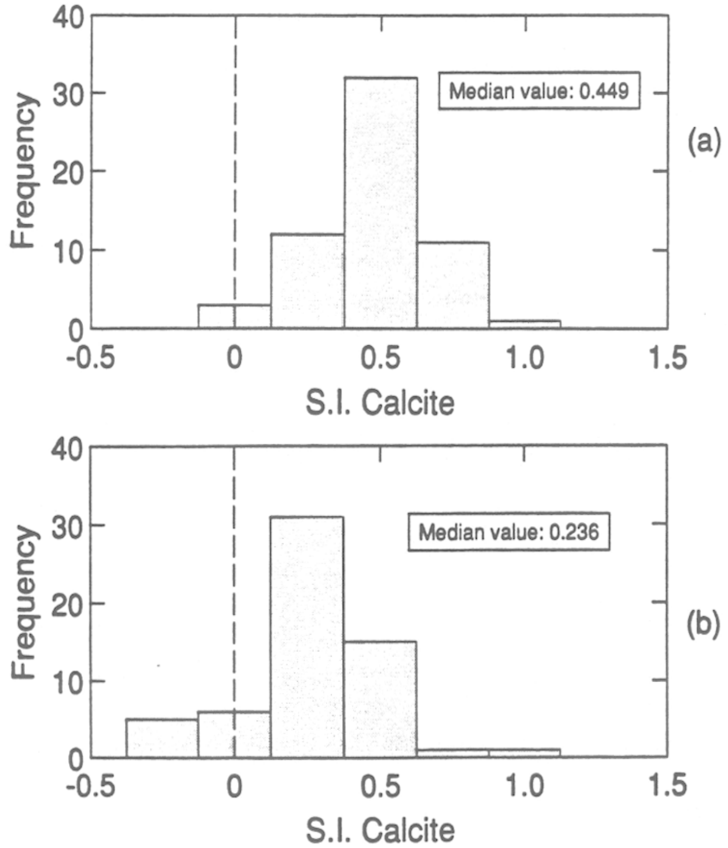
II — RESULTS

1. Stripa data : sensitivity of calcite and fluorite S.I. values

Variations in the calcite S.I. values will be most affected by uncertainties in the calcium concentration, the alkalinity and the pH if the thermodynamic properties are reasonably precise and consistent. Uncertainties of 10 % were assumed for calcium concentration and alkalinity and an uncertainty of 0.2 was assumed for the pH. From inter-laboratory comparisons and other evaluations of the Stripa groundwater analyses, 10 % uncertainty on analytical determinations was an upper limit in most instances. It is not possible to assign an error on each individual constituent determination any better than that because of the complex factors that enter into it. The pH measurements had uncertainties of less than 0.1 unit but contamination by CO_2 absorption from the air could cause greater error in the accuracy. For the worst case situation, it was further assumed that these errors had all accumulated in the direction that would decrease the S.I. for calcite. The histogram plot of the original data is shown in figure 2a and the test case, incorporating all the analytical errors, is shown in figure 2b. The median calcite S.I. decreased by 0.22 (log units) yet the median value and the greater majority of values still are clearly supersaturated. To determine the likelihood of such a cumulative error in this data set, histograms portraying the charge imbalance distribution before and after the incorporation of the analytical uncertainties are plotted in figures 3a and 3b, respectively. The charge imbalance is defined by the following formula :

$$\text{Charge balance } (\%) = \frac{(\Sigma \text{ meq cations} - \Sigma \text{ meq anions})\text{x}100}{(\Sigma \text{ meq cations} + \Sigma \text{ meq anions})/2}$$

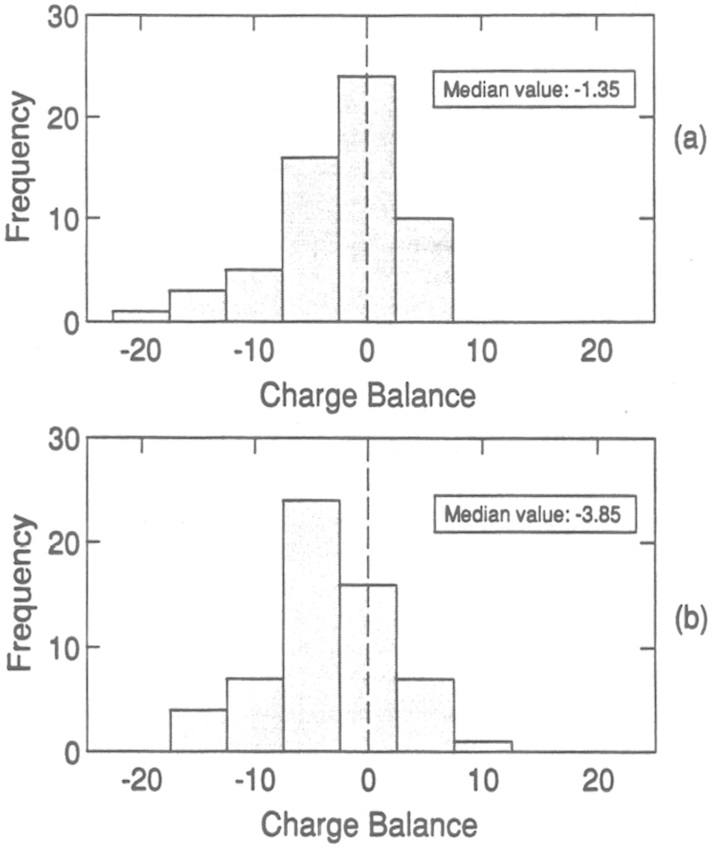
The shift in the charge imbalance by 2.5 % is strong evidence that the accumulated error is unlikely. Consequently, we must conclude that the supersauration with respect to calcite by nearly one-half an order of magnitude is real and must be due to solid-solution behavior or kinetics. Since analyzed calcites from the Stripa granite have been found to be rather pure (Shaun FRAPE, pers. comm.) it is more likely, in this instance, that kinetic effects are inhibiting calcite solubility equilibium.



— Figure 2 —

S.I. calcite for Stripa groundwaters - a : original data ; b : test data.

Indices de saturation S.I. de la calcite pour les eaux souterraines de Stripa - a : données originales ; b : données tests.



— Figure 3 —

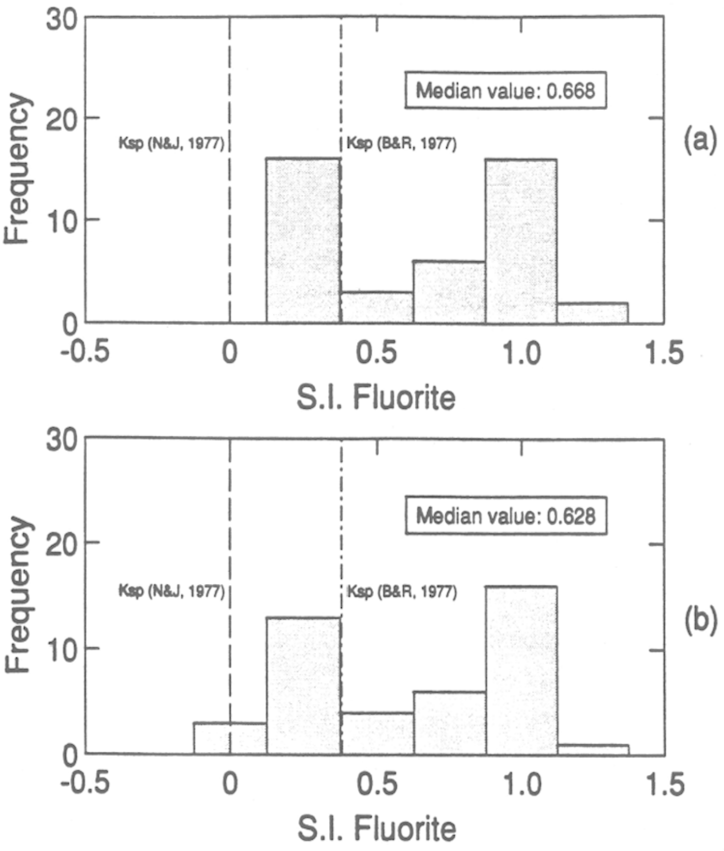
Charge balance for Stripa groundwaters - a: original data ; b : test data.

Balance ionique pour les eaux souterraines de Stripa. a : données originales ; b : données tests.

The thermodynamic values that were used to compute both IAP and S.I. values for calcite were obtained from the work of PLUMMER and BUSENBERG (1982). The uncertainties attached to their equilibrium constants were carried through the speciation and S.I. calculations and were found to decrease the S.I. by about 0.15 if accumulated in the same direction, for the worst-case scenario. Thus, if the maximum thermodynamic errors are combined with the maximum analytical errors, it is possible to bring many of the data points to saturation equilibrium. When this is done, however, the results are clearly biased and the charge balance deteriorates. If truly random errors had been chosen, the results would not appear much different from the original data set.

The results for fluorite S.I. values are similar to those for calcite except that they are much less sensitive to pH uncertainty and much more sensitive to the Ksp for fluorite, which is not known nearly as well as that for calcite. Furthermore, the distribution of S.I. values for fluorite is much more dispersed than that for calcite. The maximum range error likely in the Ksp for fluorite is about 0.38 log units based on Ksp data from table I. The change in the histogram with accumulated 10 % uncertainties in calcium concentration and fluoride concentration is apparent in figures 4a and 4b. The probable range in the Ksp is shown by an additional dotted line at 0.38 S.I. Uncertainties in the other equilibrium constants were tested but had little effect on the S.I. values. Once again the results indicate a real supersaturation for fluorite that cannot be accounted for by analytical or thermodynamic uncertainties.

The sensitivity of an S.I. to different input variables (e.g. analytical concentrations) can be estimated by looking at the effect of a single parameter uncertainty and calculating a sensitivity factor for that variable. The sensitivity factor is the partial derivative of the S.I. with respect to the input variable. Since all the input concentrations were modified by a constant amount (10 %), only the change in S.I. need be compared. For the example with calcite there would be three sensitivity factors related to input concentrations, one for calcium, one for alkalinity and one for pH. A comparison of these sensitivities indicates that the S.I. for calcite is most sensitive to uncertainties in pH. The sensitivity ordering sequence is pH $\leqslant$ alkalinity $\leqslant$ calcium. Table III summarizes the sensitivity of the S.I. values to single parameter uncertainties for one water analysis from the Stripa group and one analysis from the Leviathan group.



— Figure 4 —

S.I. fluorite for Stripa groundwaters - a : original data ; b : test data.

Indices de saturation S.I. de la fluorine pour les eaux souterraines de Stripa - a : données originales ; b : données tests.

Table III

Sensitivities of saturation indices to input variables

Sensibilité des indices de saturation aux variables d'entrée

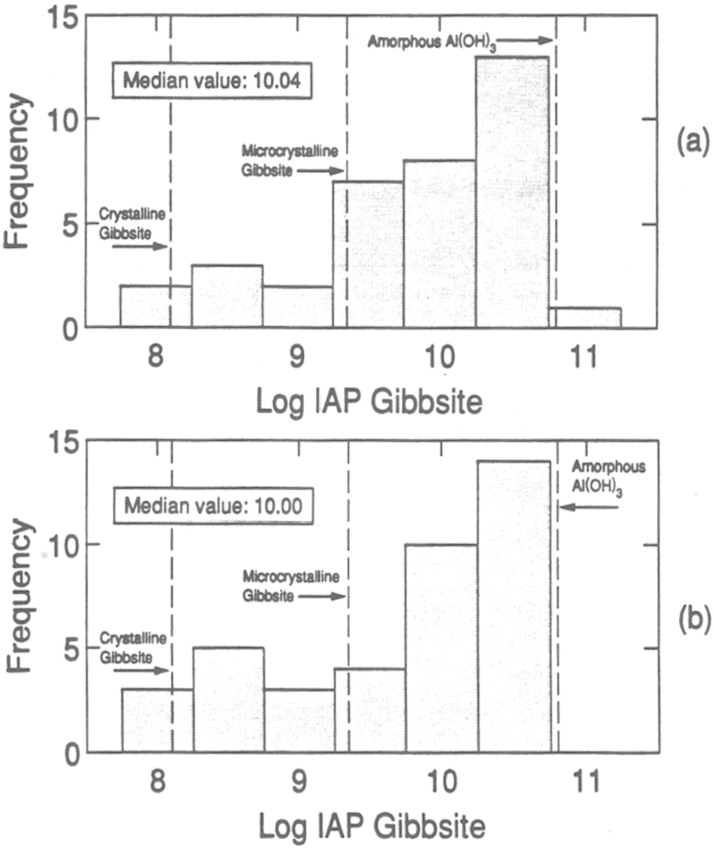
Change of Input Variable	Saturation Indices[1]				
	Stripa		Leviathan		
	calcite	fluorite	barite	gibbsite	ferrihydrite
original	0.426	1.04	0.480	0.594	0.298
ΔCa(10%)[2]	0.392	0.996	-	-	-
ΔHCO_3	0.366	-	-	-	-
ΔF(10%)	-	0.945	-	-	-
ΔAl(10%)	-	-	-	0.520	-
ΔFe(10%)	-	-	-	-	0.252
ΔSO_4	-	-	0.451	-	-
ΔBa(10%)	-	-	0.433	-	-
ΔpH(0.2)	0.318	-	-	0.272	0.097
ΔSum	0.228	0.904	0.405	0.192	0.052

[1] The calcite and fluorite S.I. values are taken from one analysis of Stripa groundwater typical of the deep groundwaters (borehole V1-840111). The remaining S.I. values are taken from a sample about midpoint in the Leviathan mine drainage system.

[2] The delta values refer to a decrease in the input variable by the amount shown in parentheses. The delta sum value refers to a decrease in all input variables listed in the column above by the amounts shown.

2. Leviathan data for gibbsite, ferrihydrite and barite

Gibbsite solubility can cover a wide range of values depending on grain size and degree of crystal perfection. Therefore the IAP values have been plotted in the histograms in figures 5a and 5b rather than the S.I. values and the solubilities of three varieties of gibbsite (crystalline from MAY *et al.*, 1979, microcrystalline from HEM and ROBERSON, 1967, and amorphous from FEITKNECHT and SCHINDLER, 1963) are indicated by the vertical dashed lines. Most of the experimental values lie between the published values for microcrystalline gibbsite and amorphous gibbsite, which is exactly what would be expected in a stream system that is known to be actively precipitating an amorphous hydrated aluminum solid phase (NORDSTROM *et al.*, 1984). Although these waters appear to be supersaturated with respect to crystalline gibbsite, they do not appear to be supersaturated with respect to the most soluble form of $Al(OH)_3$. This pattern is consistent with what many researchers have observed in acidified surface waters (DRISCOLL *et al.*, 1984 ; NORDSTROM and BALL, 1986).



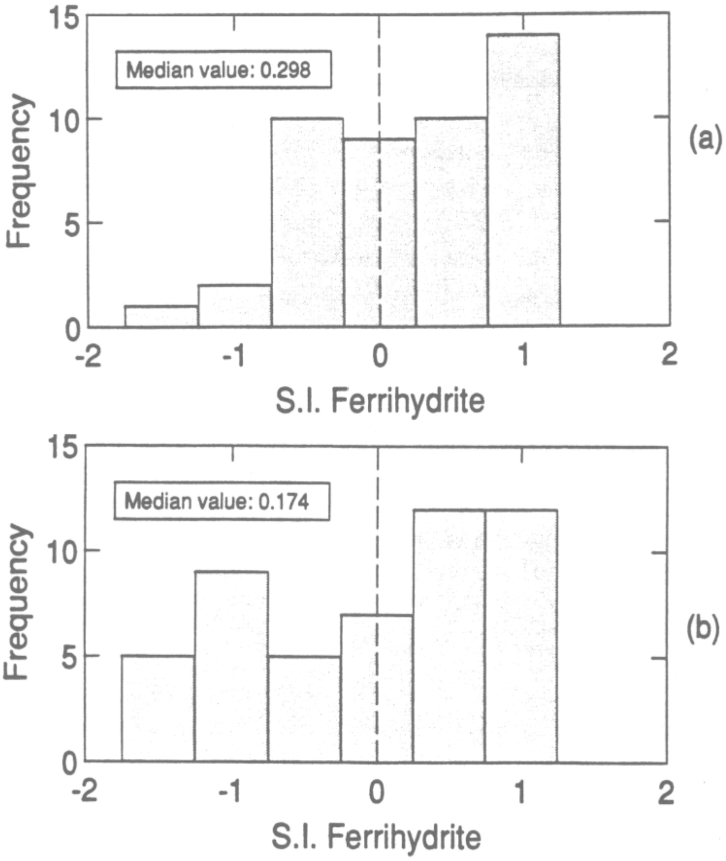
— Figure 5 —

Log IAP gibbsite for Leviathan surface waters - a : original data ; b : test data.

Log IAP gibbsite pour les eaux de surface de Leviathan. a : données originales ; b : données tests.

The sensitivity of the gibbsite IAP depends primarily on the analytical uncertainty in pH and aluminum concentration and not on the thermodynamic uncertainties, if the relationship between gibbsite Ksp and degree of crystallinity is accepted. A recent review of the equilibrium data for mononuclear aluminum speciation indicates that most of the data have uncertainties smaller than those necessary for reliable speciation calculations (NORDSTROM and MAY, 1989). Sensitivities for gibbsite S.I. values should also take into account the method employed to determine dissolved aluminum and organically-bound aluminum, if applicable. Organic-aluminum complexing is often important in low ionic strength waters (DRISCOLL *et al.*, 1984).

Ferric hydroxide solubility also can cover a wide range depending on grain size, crystallinity and phase type. The value of 37 (or — 5.0 with protons in the reactions) used for the pKsp of ferrihydrite is the most soluble value obtained by several different investigators (e.g. LAMB and JACQUES, 1938 ; BIEDERMANN and SCHINDLER, 1957 ; LANGMUIR and WHITTEMORE, 1971). Although the presence of ferrihydrite was not determined, there is ample evidence that it is the actively precipitating phase in acid mine waters (SCHWERTMANN, 1985 ; FERRIS *et* *al.*, 1989) and that amorphous ferric hydroxide may not exist. The histograms plotted for ferrihydrite (fig. 6a and 6b) show up to one order of magnitude supersaturation. Propagated uncertainties from thermodynamic data cannot account for an order of magnitude of supersaturation. The test data (fig. 6b) include a 10 % decrease in dissolved Fe(III) and a 0.2 unit decrease in pH. The result, a 0.12 unit decrease in the S.I., is not sufficient to explain the high supersaturation. There are five possible explanations for this amount of supersaturation : (1) organic-iron complexing, (2) incomplete removal of colloidal particles by filtration during field sampling, (3) the presence of high dissolved aluminum concentrations that tend to increase the IAP for ferrihydrite (Whittemore, 1973), (4) an unknown kinetic effect associated with acid mine drainage that inhibits nucleation and precipitation and (5) inhibition of colloid formation by iron-sulfate complexes (Music *et al.*, 1982). Field filtering experiments carried out by the U.S. Geological Survey (Briant Kimball, pers. comm.), indicate that significant quantities of colloidal iron will pass through membrane filters and could lead to apparent supersaturation effects. Possible uncertainty propagated by errors in sulfate determinations has been examined because sulfate has the greatest capacity to complex iron in these stream waters. No detectable change in the median S.I. for ferrihydrite was found when the sulfate concentration was decreased by 10 %.

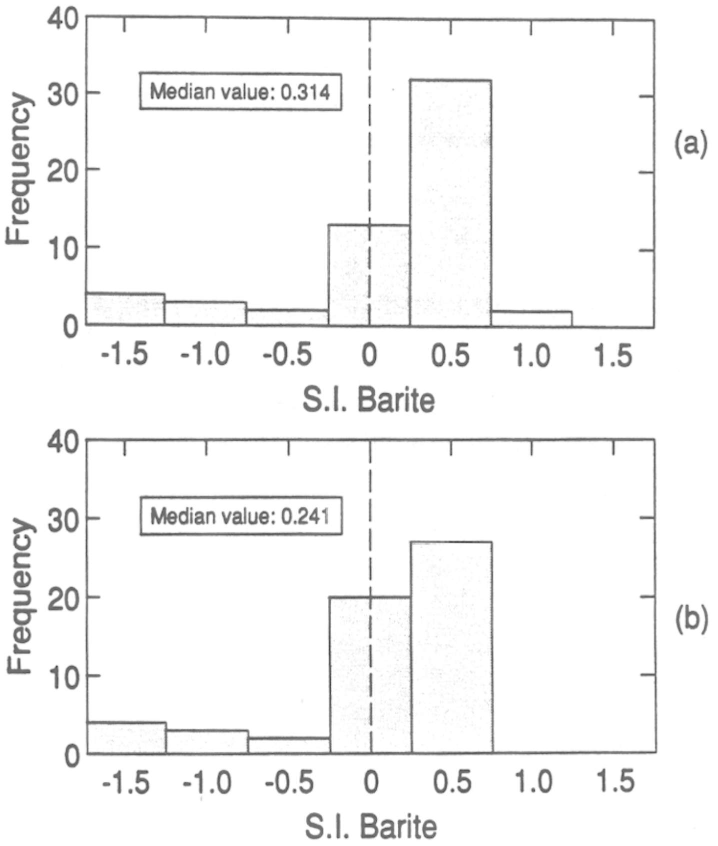


— Figure 6 —

S.I. ferrihydrite for Leviathan surface waters - a : original data ; b : test data.

Indices de saturation S.I. de la ferrihydrite pour les eaux de surface de Leviathan - a : données originales ; b : données tests.

The median S.I. for barite, shown in figures 7a and 7b, decreases only by 0.07 with a 10 % decrease in both barium and sulfate concentrations. The Ksp for barite is one of the better known equilibrium constants and uncertainties in this parameter cannot account for the extent of supersaturation. The tentative conclusion is that this degree of supersaturation, up to one-half an order of magnitude, is a kinetic effect similar to that for calcite in the Stripa groundwater. Inclusion of the $BaSO_4^\circ$ ion pair can, however, make a noticeable difference in the S.I. for barite. The median barite S.I. was decreased by 0.225 after incorporating the ion pair into the computations, using pK = 2.7 (Smith and Martell, 1976). Figures 7a and 7b both have the $BaSO_4^\circ$ ion pair in the computations. We conclude that, in high sulfate waters, this ion pair should be included.



— Figure 7 —

S.I. barite for Leviathan surface waters - a : original data ; b : test data.

Indices de saturation S.I. de la baryte des eaux de surface de Leviathan - a : données originales ; b : données tests.

III — CONCLUSIONS

A sensitivity analysis, performed on two groups of water analyses for the saturation states of five minerals (calcite, fluorite, gibbsite, ferrihydrite and barite), demonstrates that supersaturation does commonly occur and cannot be accounted for by analytical and thermodynamic uncertainties. The reason for supersaturation is not the same for all the mineral saturation states.

1. Calcite supersaturation cannot be accounted for by grain size / crystallinity effects, nor by solid solution solubility behavior, organic complexes or uncertainties in the database. A kinetic effect seems to be the most likely explanation.

2. Fluorite supersaturation is partly, but not totally, due to uncertainties in the Ksp. A kinetic effect also must be operative for fluorite.

3. Gibbsite supersaturation can be fully accounted for by degree-of-crystallinity effects on solubility, and/or by organic complexes and/or by normal data base uncertainties. No significant supersaturation with respect to the most soluble $Al(OH)_3$ precipitate (amorphous) has been observed.

4. Ferrihydrite supersaturation up to one order of magnitude has been observed and is not well understood. Possible reasons for supersaturation include :
- degree-of-crystallinity effects ; colloidal iron particles are well-known to be smaller than the pore size of standard field filtration membranes ;
- soluble organic-iron complexes ;
- inhibiting presence of high dissolved aluminum concentrations ;
- inhibition by $Fe(III)$-SO_4 complexes.

5. Barite supersaturation frequently can result if the $BaSO_4^{\circ}$ ion-pair is not included in the equilibrium speciation computations. When this ion-pair is included, however, barite still can be significantly oversaturated in natural waters. This phenomenon is probably a result of the slow rate of nucleation and growth relative to the stream flow rate. For example, more than 2 orders of magnitude supersaturation is needed for homogeneous nucleation of barite (NIELSEN, 1961).

Further sensitivity analyses may prove useful as a guide to how precise and consistent thermodynamic data must be for purposes of chemical modeling. A systematic appraisal could be made on the propagation of errors from thermodynamic data to determine what are acceptable uncertainties for reliable chemical modeling results.

Finally, chemical equilibrium computations are a necessary tool to determine whether or not mineral saturation is reached in natural waters. These computations have shown for one set of groundwater analyses and another set of surface water analyses that a mineral solubility control is apparent even though supersaturation states are commonly encoutered. Such conditions should be optimal for mineral precipitation and, in some cases, a steady state may have been reached between the rate of precipitation and the input rate of reactive ions, such as the rate of oxidation of dissolved iron in acid mine waters or the transport rate of a saline source into a groundwater system where calcite is precipitating.

For chemical modeling of natural waters there are three essential ingredients that are evident from these investigations : (1) water analyses must be very carefully done so that constituents are determined to an uncertainty no greater than about 10 %, (2) assumptions and uncertainties in the thermodynamic data need to be known and (3) the mineralogy, especially degree-of-crystallinity and identification of the smallest particles, must be known.

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