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# Error Propagation in Geochemical Calculations of Groundwater-Mineral Interactions: A Case Study from the Pingdingshan Coalfield, Henan

WANG Guangcai, TAO Shu,

*Department of Urban and Environment Sciences, Peking University, Beijing 100871*

SHEN Zhaoli and ZHONG Zuoshen

*Department of Environment Sciences, China University of Geosciences, Beijing 100083*

**Abstract**    The WATEQ4F-based "multiple step method", or the method of running WATEQ4F repeatedly, was used to evaluate the error propagation in computations of water-mineral interactions under the circumstances of constant and varied temperatures due to the uncertainties of input variables. The results show the following: the errors of water chemistry analysis can strongly affect the modelling results of water-mineral reactions; different input variables (errors) have different effects on the saturation indices (S.I.) of different minerals; in many cases, the S.I. errors of minerals change with temperatures.

**Key words:**    water-minerals interactions, error propagation, temperature, WATEQ4F

## 1   Introduction

Mathematical modelling is one of the main approaches to the quantitative study of water-mineral interactions in groundwater systems. In combination with the knowledge of mineralogy, hydrogeology and isotopes, the modelling can be a very useful tool in the interpretation of the hydrogeochemical evolution and geological structure of aquifer systems (Plummer, 1994; and Wang et al., 1998). So far, more than 50 models of water-mineral reaction equilibrium, or speciation models, have been developed and documented (Bassett and Melchior, 1990; Mangold, 1991). Using speciation modelling such as WATEQ4F (Ball and Nordstrom, 1991) we can generally conduct the computations of distribution and activities of aqueous species and the saturation indices (S.I.) of groundwater with regard to minerals. Before those codes are put into practice, it is necessary to evaluate the validity of the models for user's specific research objects. Despite the wide application of geochemical models, the error propagation of modelling, which should be a part of assessment of the validation of models, has not been adopted as a routine part of a geochemical investigation (Tsang, 1991; Criscent et al., 1996).

Two sources of uncertainty are usually concerned in geochemical computations: uncertainty in thermodynamic data and analytical uncertainty in measured concentrations of components (Criscent et al., 1996; Schecher and Driscoll, 1987). Nordstrom (1989) used the WATEQ4F-based (MST), i.e. the method of running WATEQ4F repeatedly, to calculate and analyze the effects of both the change of input hydrochemical variables and thermodynamic data on the computed S.I. of calcite and fluorite from a crystalline groundwater at Stripa, Sweden, and that of barite, gibbsite, and ferrihydrite from a surface water receiving the acid mine drainage in the Leviathan basin, California (Nordstrom and Ball, 1989). Anderson (1976) and Xu and Yao (1990) calculated the free energy of a compound, a reaction equilibrium temperature and sulphide solubilities and isotopic abundances of several elements by the Monte-Carlo method respectively. Schecher and Driscoll (1987, 1988) combined the Monte-Carlo method with an acidification chemical equilibrium model to evaluate the propagation of uncertainties in both thermodynamic and analytical data. Criscenti et al. (1996) conducted combined computations of the Monte-Carlo method and generalized sensitivity analysis (GSA) to examine the significance of

thermodynamic and analytical uncertainties in predicted pH values for a sodium bicarbonate buffer solution and for calcite saturation indices in the system $Ca-CO_3-Na-Cl-H_2O$ based on the geochemical model, GA (Criscenti et al., 1996). To date, however, the effects of error propagation on most of the computed outputs, especially that related to the temperature uncertainty, have not been well known.

In this paper, the MST is employed to compute the error propagation and sensitivity analysis of input data uncertainties through the code WATEQ4F under different scenarios including constant and varied temperatures based on water samples from a Cambrian karst aquifer in the Pingdingshan coalfield, China. The study is aimed at obtaining a further understanding of error propagation especially through temperature uncertainty, and gathering further information about the groundwater systems.

## 2 Hydrogeological Setting

The Pingdingshan coalfield is located in the southwestern part of Henan province, central China (Wang Rennong, 1995; Zhong et al., 1998). Twelve coal mines, named Nos. 1 to 12, cover a total area of about 400 km² in the coalfield. The topography rises from 80 m above sea level in the northeast to 150 m in the southwest. The Baiguishan reservoir is situated in the southwestern part and the Zhanhe River flows from west to east through the southern part of the area. The Guodishan fault is the largest one of the area. Quaternary alluvial deposits, Permo-Carboniferous thin-bedded limestone and sandstone and Cambrian limestone (karst) are main water-bearing strata. Among them Cambrian limestone, which is exposed locally in the southwestern hilly land covering an area of 20 km², forms the most important karst aquifer characterized by its enormous thickness and extensive distribution. According to previous studies, the Cambrian karst groundwater system can be divided into two subsystems, i.e. the southwest and northeast subsystem, with the Guodishan fault as their interior boundary based on the indices of water temperature, water level, water yield and water chemistry (Wang et al., 1998).

## 3 Calculation Scenarios

Error propagation was computed using the similar approach to that of Nordstrom and Ball (1989), that is, the WATEQ4F-based MST. The WATEQ4F was run repeatedly to obtain the effects of input data errors on the outputs. Two scenarios were considered: one was that of varying a variable each time, while keeping others unchanged; the other was that of varying all variables at one time. Through those computations not only the effects of different individual variables on outputs but also the "comprehensive error propagation" were obtained and evaluated. Input variables included Ca, Mg, Na, K, Cl, $SO_4$, $HCO_3$, $SiO_2$, pH, $T$ (temperature) etc., and the values of analytical errors 5% and 10%, 0.2 and 2 °C were taken for the chemical compositions, pH and $T$ respectively, based on the study purpose, experimental instructions and experience both in the laboratory and field.

A typical water sample collected from underground workings in coal mine No. 8 was selected as a computed sample. The water temperature (36 °C), water regime and water chemistry keep stable basically at the water point for many years according to the long-term regime observations. Two cases of computations were conducted: one is using real data (including the water temperature) to evaluate the error propagation

**Table 1  Computed S.I. of minerals with different input errors**

| Input data error | Saturation indices | | | | |
|---|---|---|---|---|---|
| | Calcite | Dolo-mite | Gypsum | Chalce-dony | Quartz |
| Original data | 0.741 | 1.148 | −1.557 | 0.023 | 0.419 |
| $\triangle Ca^{2+}$ (5%) | 0.720 | 1.127 | −1.577 | 0.023 | 0.419 |
| $\triangle Mg^{2+}$ (5%) | 0.742 | 1.129 | −1.555 | 0.023 | 0.419 |
| $\triangle HCO_3^-$ (5%) | 0.721 | 1.107 | −1.555 | 0.023 | 0.419 |
| $\triangle SO_4^{2-}$ (5%) | 0.744 | 1.155 | −1.576 | 0.023 | 0.419 |
| $\triangle SiO_2$ (5%) | 0.741 | 1.148 | −1.557 | −0.010 | 0.385 |
| $\triangle Ca^{2+}$ (10%) | 0.702 | 1.109 | −1.594 | 0.023 | 0.419 |
| $\triangle Mg^{2+}$ (10%) | 0.742 | 1.103 | −1.552 | 0.023 | 0.419 |
| $\triangle HCO_3^-$ (10%) | 0.700 | 1.064 | −1.553 | 0.023 | 0.419 |
| $\triangle SO_4^{2-}$ (10%) | 0.749 | 1.118 | −1.592 | 0.023 | 0.419 |
| $\triangle SiO_2$ (10%) | 0.741 | 1.148 | −1.557 | −0.022 | 0.374 |
| $\triangle pH$ (0.2) | 0.542 | 0.748 | −1.554 | 0.026 | 0.422 |
| $\triangle T$ (2 °C) | 0.717 | 1.077 | −1.556 | 0.046 | 0.447 |
| $\triangle Sum\ 1$ (5%)* | 0.505 | 0.676 | −1.587 | −0.004 | 0.392 |
| $\triangle Sum\ 2$ (10%)** | 0.466 | 0.594 | −1.623 | −0.020 | 0.376 |

*, **: $\triangle Sum\ 1$ (5%) and $\triangle Sum\ 2$ (10%) indicate that the analytical errors for all the chemical components are taken as 5% and 10% respectively.

and states of water-minerals at the point at a specific temperature; the other is using the same sample at several assumed temperatures so as to assess the variations of error propagation at different temperatures.

## 4 Computations Based on Real Data

The main chemical composition of the water sample is (ionic concentrations in mg/l): $Ca^{2+}$ (55.71), $Mg^{2+}$ (29.78), $Na^+$ (121.03), $K^+$ (13.98), $Cl^-$ (58.50), $SO_4^{2-}$ (188.64), $HCO_3^-$ (347.80) and $SiO_2$ (24.00), with pH=7.90 and water temperature =36°C. The main outputs (S.I. of several minerals) computed by running WATEQ4F are shown in Table 1 with the input analytical errors 5% or 10%, 0.2 and 2°C for the chemical compositions, pH and $T$ respectively.

All the above computations were conducted at a temperature of 36°C except for "$\triangle T$ (2°C)", "$\triangle$Sum 1 (5%)" "and $\triangle$Sum 2 (10%)". Compared with the S.I. computed with the original data, the results obtained with different input error cases (i.e. varying only one variable each time and varying all variables at one time) are not changed significantly; in other words, the related computations and extension analysis in previous studies are reliable from the view-point of input data error propagation (water samples were collected repeatedly in this field trip). In order to obtain the effect degrees of different input variables with the same error (%) on the S.I. of different minerals, the calculations were performed based on the data of

**Table 2    Input variable error and S.I. error**

| Input variable error | S.I. error | | | | |
|---|---|---|---|---|---|
| | Calcite | Dolo-mite | Gypsum | Chalce-dony | Quartz |
| $\triangle Ca^{2+}$ (5%) | 0.021 | 0.021 | 0.020 | 0.000 | 0.000 |
| $\triangle Mg$ (5%) | -0.001 | 0.019 | -0.002 | 0.000 | 0.000 |
| $\triangle HCO_3^-$ (5%) | 0.020 | 0.041 | -0.002 | 0.000 | 0.000 |
| $\triangle SO_4^{2-}$ (5%) | -0.003 | -0.007 | 0.019 | 0.000 | 0.000 |
| $\triangle SiO_2$ (5%) | 0.000 | 0.000 | 0.000 | 0.033 | 0.034 |
| $\triangle Ca^{2+}$ (10%) | 0.039 | 0.038 | 0.037 | 0.000 | 0.000 |
| $\triangle Mg^{2+}$ (10%) | -0.001 | 0.044 | -0.005 | 0.000 | 0.000 |
| $\triangle HCO_3^-$ (10%) | 0.041 | 0.084 | -0.004 | 0.000 | 0.000 |
| $\triangle SO_4^{2-}$ (10%) | -0.008 | 0.030 | 0.035 | 0.000 | 0.000 |
| $\triangle SiO_2$ (10%) | 0.000 | 0.000 | 0.000 | 0.045 | 0.045 |
| $\triangle pH$ (0.2) | 0.199 | 0.400 | -0.003 | -0.003 | -0.002 |
| $\triangle T$ (2°C) | 0.024 | 0.071 | -0.001 | -0.023 | -0.028 |
| $\triangle$Sum 1 (5%)* | 0.236 | 0.472 | 0.030 | 0.027 | 0.027 |
| $\triangle$Sum 2 (10%)** | 0.275 | 0.554 | 0.066 | 0.043 | 0.043 |

*, **: Indications same as in Table 1.

**Table 3    Sensitivity factors of S.I. of different minerals**

| Imput variable | Sensitivity factor | | | | |
|---|---|---|---|---|---|
| | Calcite | Dolomite | Gypsum | Chalcedony | Quartz |
| $Ca^{2+}$ | 0.0070 | 0.0068 | 0.0061 | – | – |
| $Mg^{2+}$ | – | 0.0148 | – | – | – |
| $HCO_3^-$ | 0.0012 | 0.0024 | – | – | – |
| $SO_4^{2-}$ | – | – | 0.0019 | – | – |
| $SiO_2$ | – | – | – | 0.0188 | 0.0188 |
| pH | 0.0995 | 0.2000 | -0.0015 | -0.0015 | -0.0010 |
| $T$ | 0.0120 | 0.0355 | -0.0005 | -0.0115 | -0.0117 |

Table 1 and the results are presented in Table 2.

The data in Table 2 show the following: (1) When the error values of the chemical composition, pH and $T$ are 10%, 0.2 and 2°C respectively, the "comprehensive errors" ($\triangle$Sum 2 (10%)) of the computed S.I. are: calcite 0.275, dolomite 0.554, gypsum 0.066, chalcedony 0.043 and quartz 0.043, of which the S.I. error of calcite is close to that reported by others (Nordstrom and Ball, 1989) and the errors of the rest minerals are presented firstly in this paper. (2) For a specific mineral, the "comprehensive error" of the S.I. is not a simple algebraic sum of the errors caused by individual variables, i.e., the "comprehensive error" is not the "worst scenario". (3) The main sources of the S.I. errors of minerals are: calcite: pH, $HCO_3^-$, $Ca^{2+}$ and $T$; dolomite: pH, $HCO_3^-$, $T$, $Mg^{2+}$ and $Ca^{2+}$; gypsum: $Ca^{2+}$ and $SO_4^{2-}$; chalcedony: $SiO_2$ and $T$; quartz: $SiO_2$ and $T$.

By defining the sensitivity factors as the partial derivatives of the S.I. with respect to input variables (which here indicate the changed values of the S.I. relative to those of the chemical compositions (1 mg/l), pH (0.1) and $T$ (1°C) respectively), the data in Table 3 can be obtained from the data in Table 2 and the original analytical information.

There are 4, 5, 4, 3 and 3 sensitivity factors for calcite, dolomite, gypsum, chalcedony and quartz respectively. The order of decreasing values of the factors is: calcite: pH>$T$>$Ca^{2+}$>$HCO_3^-$; dolomite: pH>$T$>$Mg^{2+}$>$Ca^{2+}$>$HCO_3^-$; gypsum: $Ca^{2+}$>$SO_4^{2-}$>pH>$T$; chalcedony and quartz: $SiO_2$>$T$>pH. To evaluate the calculation reliability of the factors in Table 3, the factors of the S.I. of calcite and dolomite with respect to pH, 0.0995 and 0.2000, are taken as examples. The two factors are in accordance with the theoretically deduced values reported by the
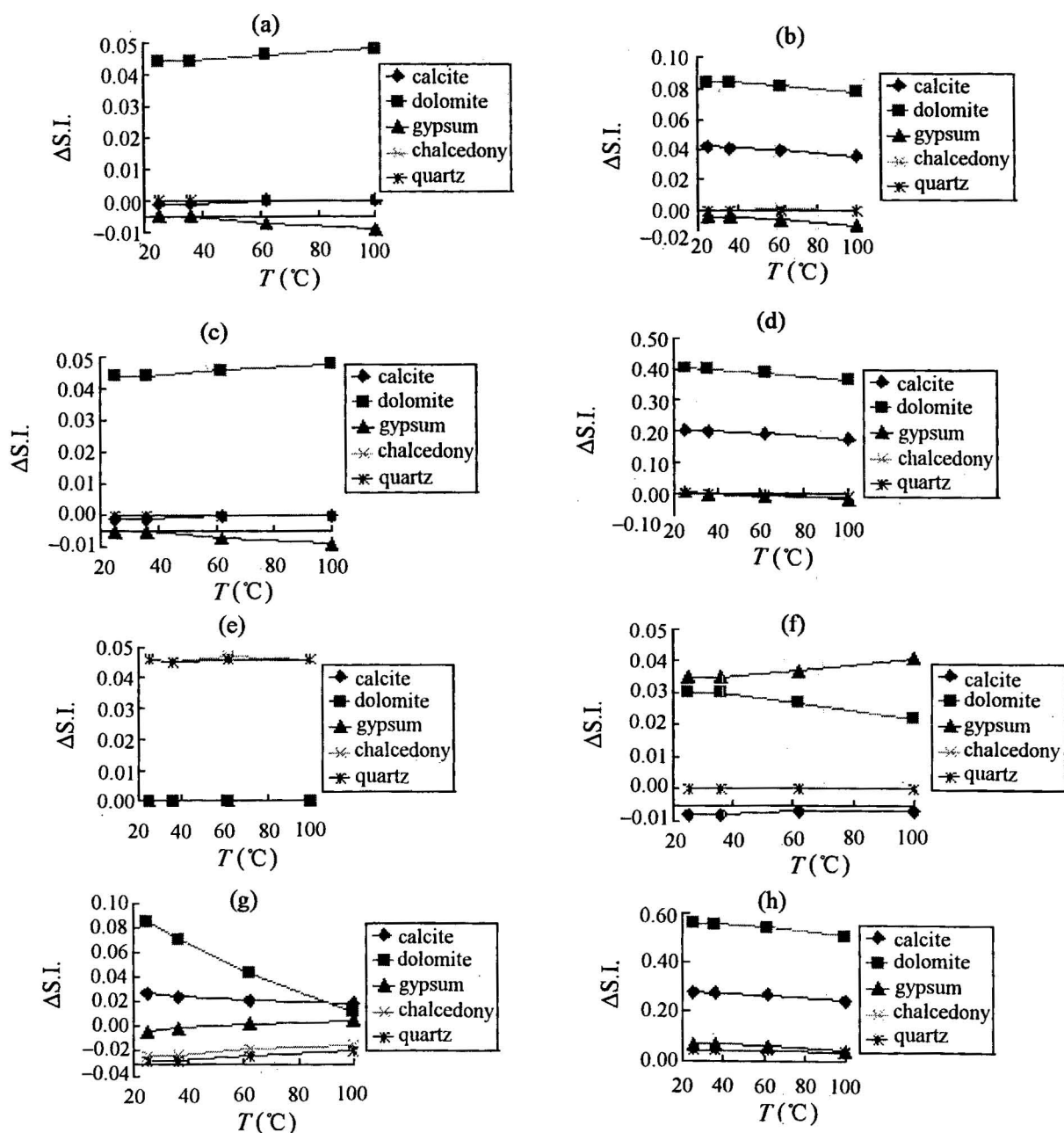
Fig. 1.   Trends of variation of the S.I. errors at different temperatures.

(a)–(g) represent respectively the cases when the errors of individual chemical compositions, pH and $T$ are taken as 10%, 0.1 and 1℃ while others keep unchanged. (a)–$Ca^{2+}$, (b)–$HCO_3^-$, (c)–$Mg^{2+}$, (d)–pH, (e)–$SiO_2$, (f)–$SO_4^{2-}$, (g)–$T$ and (h)–all of the input variables are changed.

USGS (1994).

## 5   Analysis of S.I. Error Variations at Different Temperatures

Most of the above computations were conducted at a temperature of 36℃. To understand the variation of

error propagation at different temperatures, again, the WATEQ4F was run repeatedly with the input data of the same sample at temperatures of 25°C, 62°C and 100℃. We selected 25°C and 100℃ is because they are two ends of the "suitable temperature range" for WATEQ4F, while 62℃ is the temperature of deep water estimated by the chalcedony geothermometer

(Wang, 1996). The computations at the temperatures were conducted in similar ways to that at 36℃. Based on the computed results and the data in Table 2, the relationships between the errors of S.I. of different minerals and temperatures at constant errors of individual input variables can be got and shown in Figure 1.

It is shown in Figure 1 that when the errors of individual variables keep constant without considering the errors of other variables, with in the temperature range of 25–100℃, the variation trends of the S.I. errors are:

(1) The error of $Ca^{2+}$ keeps constant (10%), and with increasing temperature, the errors of $S.I._{dolomite}$ ($\triangle S.I._{dolomite}$) and $\triangle S.I._{quartz}$ remain unchanged, and the increasing or decreasing trends of the errors of $\triangle S.I._{calcite}$, $\triangle S.I._{gypsum}$ and $\triangle S.I._{chalcedony}$ are negligible.

(2) The error of $HCO_3^-$ keeps constant (10%), and with increasing temperature, the errors of $\triangle S.I._{calcite}$ and $\triangle S.I._{dolomite}$ decrease and that of $\triangle S.I._{gypsum}$ increases.

(3) The error of $Mg^{2+}$ keeps constant (10%), and with increasing temperature, the errors of $\triangle S.I._{dolomite}$ and $\triangle S.I._{gypsum}$ increase negligibly.

(4) The error of pH keeps constant (0.1), and with increasing temperature, the errors of $\triangle S.I._{calcite}$ and $\triangle S.I._{dolomite}$ decrease, and those of $\triangle S.I._{gypsum}$, $\triangle S.I._{chalcedony}$ and $\triangle S.I._{quartz}$ increase.

(5) The error of $SiO_2$ keeps constant (10%), and with increasing temperature, the S.I. errors of all minerals are not changed.

(6) The error of $SO_4^{2-}$ keeps constant (10%), and with increasing temperature, the error of $\triangle S.I._{dolomite}$ decreases and that of $\triangle S.I._{gypsum}$ increases.

(7) The error of $T$ keeps constant (1℃), and with increasing temperature, the errors of $\triangle S.I._{calcite}$, $\triangle S.I._{dolomit}$, $\triangle S.I._{chalcedony}$ and $\triangle S.I._{quartz}$ all decrease.

(8) The error of all input variables keep constant (10%), and with increasing temperature, the errors of $\triangle S.I._{calcite}$, $\triangle S.I._{dolomit}$, $\triangle S.I._{gypsum}$, $\triangle S.I._{chalcedony}$ and $\triangle S.I._{quartz}$ all decrease.

## 6 Conclusions

The WATEQ4F-based MST was used to evaluate the error propagation in computations of groundwater-mineral interactions at constant and varying temperatures in the Pingdingshan coal mine. The

in the Pingdingshan coal mine. The following conclusions can be drawn.

(1) The errors of water chemistry analysis can strongly affect the results of water-mineral reaction modelling. When the error values of the chemical composition, pH and $T$ are 10%, 0.2 and 2°C respectively, the "comprehensive errors" of the computed S.I. are: calcite 0.275, dolomite 0.554, gypsum 0.066, chalcedony 0.043 and quartz 0.043. Those values of error (uncertainty) are so high that the conclusions on water-mineral interaction states can be wrong if input data errors are not considered during geochemical computations. Because of the error counteraction, the "comprehensive errors" of saturation indices of some minerals are not the "worst cases", that is, the "comprehensive errors" are not the "biggest errors".

(2) Different input variables (errors) have different effects on the saturation indices of different minerals. At a given temperature, the order of decreasing values of the sensitivity factors of S.I. of different minerals is: calcite, $pH > T > Ca^{2+} > HCO_3^-$; dolomite, $pH > T > Mg^{2+} > Ca^{2+} > HCO_3^-$; gypsum, $Ca^{2+} > SO_4^{2-} > pH > T$; chalcedony and quartz, $SiO_2 > T > pH$.

(3) In different cases, the S.I. errors of different minerals are either not changed, or decreased and increased with the variation in temperature.

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**Main references**

Anderson, G.M., 1976. Error propagation by the Monte Carlo methods in geochemical calculations. *Geochim. Cosmochim. Acta*, 40: 1533–1538.

Ball, J.W., and Nordstrom, D.K., 1991. User's manual for WATEQ4F with revised thermodynamic data base and test cases for calculating speciation of major, trace and redox elements in natural water. *U.S. Geological Survey Open File Report*, 91–183.

Bassett, R.L., and Melchior, D.C., 1990. Chemical modelling of aqueous systems. In: Melchior, D.C., and Bassett, R.L. (eds.), *Chemical Modelling of Aqueous Systems* II. ACS Symposium Series 416: 1–14.

Criscenti, L.J., Laniak, G.F., and Erikson, R.L., 1996. Propagation of uncertainty through geochemical code calculations. *Geochimica et Cosmochimica Acta*, 19: 3551–3568.

Mangold, D.C., 1991. A summary of subsurface hydrological and hydrochemical models. *Reviews of Geophysics*, 21(1): 51–79.

Nordstrom, D.K., and Ball, J.W., 1989. Mineral saturation states in natural waters and their sensitivity to thermodynamic and analytic errors. *Sci. Geol. Bull.*, 4: 269–280.

Plummer, L.N., 1994. Geochemical modelling. In: Alley, W.M. (ed.), *Regional Groundwater Quality*. New York: Van Nostrand Reinhold, 199–225

Schecher, W.D., and Driscoll, C.T., 1987. An evaluation of uncertainty associated with aluminum equilibrium calculations. *Water Resources Research*, 23: 525–534.

Schecher, W.D., and Driscoll, C.T., 1988. An evaluation of equilibrium calculations within acidification models: the effect of uncertainty in measured chemical components. *Water Resources Research*, 24: 533–540.

Tsang, C.F., 1991. Modelling process and model validation. *Groundwater*, 29(6): 825–831.

Wang, G.C., 1996. Estimation of temperatures of deep geothermal water at Pingdingshan coal mines. *Coal Geology and Explorations*, 5: 41–43 (in Chinese).

Wang, G.C., Tao, S., Shen, Z.L, and Zhong, Z.X., 1998. Geochemical modelling of groundwater in karst area and its application in Pingdingshan coal field. *Science in China (D)*, 41(4): 377–381 (in Chinese).

Wang Rennong and Li Guinchun, 1995. A discussion on coal-accumulating regularity of coal-bearing basins in China.

*Geological Review*, 41(6): 487–498 (in Chinese with English abstract).

USGS, 1994. Lecture Notes for Geochemistry of Groundwater Systems (unpublished).

Xu, L.B., and Yao, J.L., 1990. Applications of error propagation in geochemical calculations. *China Geological Sciences*, 2: 187–193 (in Chinese).

Zhong Rong and Fu Zeming, 1998. The relationship between the distribution of thick coal beds and the Late Carboniferous–early Early Permian marine transgression–regression in the north China plateform. *Acta Geologica Sinica* (Eng. ed.), 72(1): 114–120.

## About the first author

Wang Guangcai    Born in 1962; obtained a doctoral degree at the China University of Geosciences (Beijing) in 1996 and worked at the Department of Urban and Environmental Sciences, Peking University, as a postdoctoral fellow during 1997–1998. He is currently an associate professor of the Institute of Geology, China Seismological Bureau. His major research interests include geochemistry modelling and isotope study of groundwater and seismological subsurface fluids. Tel: (010) 62009012; E-mail: wanggc @pku. edu.cn. Present address: Institute of Geology, Chinese Seismological Bureau, Beijing 100029.