Use of redundant data to reduce estimation errors in geochemical speciation

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Abstract

Speciation is the process of evaluating the concentrations of all the species in a chemical system from equilibrium conditions and measured data such as total concentrations of components, electrical conductivity, pH, redox potential, gas partial pressure. It is essential for analyzing geochemical data and defining the chemical composition of waters for geochemical modeling problems like evaluating the chemical composition of evaporating, diluting, mixing waters or reactive transport. We present an algorithm that reduces estimation errors in chemical speciation calculations by means of the use of redundant data. Redundant data are measurements and assumptions that exceed the minimum data set required, and therefore are not strictly necessary, to speciate a water sample. The proposed method was compared with the classical speciation algorithm on two synthetic examples. Our re-

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sults show that using redundant data improves speciation results reducing the estimation error between computations and measurements. Moreover, the larger the amount of redundant data, the better in terms of errors of the estimated concentrations.

Keywords:

Redundant data, Geochemical modeling, Speciation, Optimization problem

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1. Introduction

Geochemical modeling is important in Earth Sciences. In particular, it is required to assess problems ranging from weathering to the characterization of the chemical composition of water and processes that could influence its quality (Appelo and Postma, 2010; Bethke, 2008). Geochemical speciation is a key step of geochemical modelling that consists of evaluating concentrations of all the species in a chemical system from measured data (e.g., total concentrations of components, pH, alkalinity, gas partial pressures, electrical conductivity, redox potential) and equilibrium constraints. For this reason, it is often termed thermodynamic speciation.

Speciation requires the solution of a non-linear system of equations and a lot of research has been focused on numerical issues that might arise when solving these equations. Several methods have been proposed to solve chemical equilibrium in a robust way in order to guarantee the convergence (Paz-García et al., 2013; Carrayrou et al., 2002; Brassard and Bodurtha, 2000) and many codes have also been released to deal with geochemical speciation calculations: GEMS3K (Kulik et al., 2013), Visual MINTEQ (Gustafsson, 2011), CHEPROO (Bea et al., 2009), ORCHESTRA (Meeussen, 2003),

19 MIN3P (Mayer et al., 2002), PHREEQC (Parkhurst et al., 1999) and its
20 interactive version, PHREEQCi (Charlton et al., 1997), EQ3NR (Wolery,
21 1983, 1992) and WATEQ4F (Ball and Nordstrom, 1991).

22 Speciation calculations are subject to implicit sources of uncertainty which
23 can derive from uncertainty in thermodynamic data, such as equilibrium
24 constant values, or from errors in chemical analyses (i.e., analytical errors).
25 These types of random errors can be referred to as "aleatory uncertainty".
26 Misjudgment in the definition of the chemical system, such as failure to ac-
27 count for some reactions or discarding others, can also lead to errors in speci-
28 ation. These can be defined as "epistemic uncertainty". They arise from an
29 incomplete or inadequate characterization of the system (Gupta et al., 2012),
30 such as assuming the neutrality of a solution when it is not electrically bal-
31 anced, or imposing equilibrium with phases that are not. The effect of errors
32 propagation in geochemical calculations has been extensively studied. In
33 particular, the effect of aleatory errors has been investigated by Weber et al.
34 (2006); Denison and Garnier-Laplace (2005); Ödegaard-Jensen et al. (2004);
35 Nitzsche et al. (2000); Cabaniss (1999, 1997); Criscenti et al. (1996); Merino
36 (1979), while Smith et al. (1999) examined the connection between aleatory
37 and epistemic errors. Although the origin and propagation effects of both
38 types of errors are different, they can be treated in the same way through
39 probability density functions, e.g., by means of mean and standard deviation
40 values.

41 All these studies use a fixed number of data to solve the speciation. Geo-
42 chemical speciation, in fact, requires a fixed minimum number of data, includ-
43 ing equilibrium assumptions, equal to the number of independent variables

of the system (i.e., number of species). For example, a carbonate system is characterized by four degrees of freedom (see Section 2.1). Therefore, four data (e.g., total concentrations of inorganic carbon and calcium, pH) or hypotheses (e.g., water activity equal to 1) are needed. However, extra data might be available (e.g., alkalinity, electrical conductivity or redox potential) or extra assumptions about the system might be made (e.g., equilibrium with calcite or $CO_{2(g)}$ in equilibrium with the atmosphere). Chemical analyses of waters, for example, often provide extra data and also the analytical errors associated to each of them.

We term these extra data as redundant and we claim that speciation calculations can benefit from their use, while acknowledging analytical errors.

The aim of this paper is to present an algorithm to include redundant data in speciation calculations and to prove that their use can improve the results by reducing estimation errors. We also claim that increasing the number of redundant data helps decreasing the estimation errors even further.

2. Methodology

We start by analyzing a speciation example to clarify the differences between the traditional and the proposed method. This allows us to formalize the problem statement and to propose a solution algorithm.

2.1. Speciation of a carbonate system

We consider the problem of calculating the concentrations of dissolved species in a carbonate system. This system has received extensive attention from the scientific community, e.g. to study seawater intrusion in carbonate coastal aquifers (Werner et al., 2013; Bear, 1999; Back et al., 1979, amongst

many others), including geochemical processes occurring in the mixing zone between freshwater and saltwater (Sanz et al., 2011; De Simoni et al., 2007; Rezaei et al., 2005), and to analyze the feasibility of CO_2 sequestration in deep aquifers (Saaltink et al., 2013; Duan and Li, 2008; Xu et al., 2006).

The most simple chemical system consists of 9 species ($N_s = 9$) and the following 5 equilibrium reactions ($N_{re} = 5$):

The number of degrees of freedom of this system is $N_s - N_{re} = 4$. This means that 4 data or assumptions are needed to solve the speciation problem. Speciation codes normally use this criterion. Optionally species with constant activity can be decoupled and eliminated, e.g., water if the system is sufficiently diluted ($a_{H_2O} = 1$) or proton if the pH is fixed ($a_{H^+} = 10^{-pH}$), to reduce the number of unknowns. Numerous methods have been proposed to eliminate constant activity species in reactive transport calculations (Kräutle, 2011; De Simoni et al., 2005; Kräutle and Knabner, 2005; Molins et al., 2004; Saaltink et al., 1998). Regardless of the decision to eliminate them, we refer generically to these methods as the traditional speciation methods, as they should all yield the same results.

Being the degrees of freedom for system (1) equal to 4, the concentrations

86 of all species can be calculated from four known data: total concentration of
 87 calcium, alkalinity, activity of water and pH for example

$$\begin{cases} Ca_{tot} : [Ca^{2+}] - x_1 = 0 \\ Alkalinity : [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] - x_2 = 0 \\ Water\ Activity : a_{H_2O} - x_3 = 0 \\ pH : -\log a_{H^+} + x_4 = 0 \end{cases} \quad (2)$$

88 where $[ ]$ represents molal concentration (mol/kgw). x_1 , x_2 and x_4 are
 89 actual measurements representing Ca_{tot} , $Alkalinity$ and pH , while x_3 is the
 90 value of water activity fixed to 1. We term these kind of equations "data
 91 equations". These must be solved together with the mass action laws deriving
 92 from system (1)

$$\mathbf{f}_{MAL} = \mathbf{S}_e \log \mathbf{a} - \log \mathbf{k} = 0 \quad (3)$$

93 where $\mathbf{a}$ is a vector containing the activities of the N_s species, $\mathbf{S}_e$ is a ma-
 94 trix ($N_{re} \times N_s$) with the stoichiometric coefficients of the equilibrium reactions
 95 and $\mathbf{k}$ is a vector (N_{re}) of equilibrium constants.

96 Generalizing the traditional speciation method we can say that $N_1 =$
 97 $N_s - N_{re}$ data equations need to be solved together with $N_2 = N_{re}$ mass
 98 action laws, $\mathbf{f}_{MAL}$:

$$\begin{cases} \mathbf{g}(\mathbf{c}) - \mathbf{x} = 0 \\ \mathbf{f}_{MAL}(\mathbf{c}) = 0 \end{cases} \quad (4)$$

99 where $\mathbf{c}$ is the vector of concentrations of the N_s species, $\mathbf{x}$ a vector of N_1
 100 data and $\mathbf{g}(\mathbf{c})$ defines operations to be applied to $\mathbf{c}$ in order to compute what

101 is measured (e.g., linear combinations of species concentrations to obtain
 102 measured components, or $-\log(\gamma_{H^+} \cdot [H^+])$ to obtain pH , where γ_{H^+} is the
 103 proton activity coefficient). Typically data equations contain balances of
 104 total concentrations, electrical charge, alkalinity, total dissolved inorganic
 105 carbon (TIC), pH values, redox potential or electrical conductivity.

106 The traditional algorithm to speciate consists of five steps: (1) dividing
 107 the species in two sets of $N_1 = N_s - N_{re}$ primary and $N_2 = N_{re}$ secondary
 108 species (Steefel and Yabusaki, 2000) with concentrations $\mathbf{c}_1$ and $\mathbf{c}_2$, respec-
 109 tively; (2) guess an initial value of primary concentrations; (3) use $\mathbf{f}_{MAL}$ to
 110 calculate $\mathbf{c}_2 = f(\mathbf{c}_1)$; (4) use data $\mathbf{x}$ to solve $g(\mathbf{c}_1, \mathbf{c}_2) - \mathbf{x} = 0$ for $\mathbf{c}_1$, (5)
 111 repeat steps (3) and (4) until convergence.

112 This work is focused on cases in which the number of available data is
 113 larger than N_1 . In this case, the resulting data equations cannot be solved
 114 exactly. Instead, they need to acknowledge measurement errors.

115 For example, if measurements of total dissolved inorganic carbon (TIC)
 116 and pressure of gas ($P_{CO_{2(g)}}$) were available and we wanted to apply zero
 117 charge balance and equilibrium with calcite as well, the data equations could
 118 be rewritten as

$$\left\{ \begin{array}{l} Ca_{tot} : [Ca^{2+}] - x_1 = \varepsilon_1 \\ Alkalinity : [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] - x_2 = \varepsilon_2 \\ Water\ Activity : a_{H_2O} - x_3 = \varepsilon_3 \\ pH : -\log a_{H^+} + x_4 = \varepsilon_4 \\ TIC : [CO_{2(aq)}] + [HCO_3^-] + [CO_3^{2-}] - x_5 = \varepsilon_5 \\ P_{CO_{2(g)}} : \log a_{CO_{2(g)}} - x_6 = \varepsilon_6 \\ Charge\ Balance : [H^+] + 2[Ca^{2+}] - [OH^-] - [HCO_3^-] - 2[CO_3^{2-}] = \varepsilon_7 \\ Calcite\ Eq. : \log a_{Ca^{2+}} + \log a_{HCO_3^-} - \log a_{H^+} - \log K_5 = \varepsilon_8 \end{array} \right. \quad (5)$$

119 where x_5 is the measured TIC , x_6 is $\log(P_{CO_{2(g)}})$ and x_7 and x_8 are
120 equal to zero because of the zero charge balance and equilibrium constraints
121 (x_7 corresponds to the saturation index of calcite, null at equilibrium). ε_i ,
122 $i = 1, \dots, 8$, represent measurement errors that need to be taken in account
123 since the system to be solved has become overdetermined (i.e., the number
124 of data is larger than N_1). The data set (5) presents 4 redundant data.

125 The algorithm to solve data equations (5) together with mass action laws
126 (3) to speciate is explained in the following section.

127 2.2. Speciation with redundant data: Problem statement

128 If redundant informations are used to solve a speciation problem, system
129 (4) can be re-defined as follows

$$\left\{ \begin{array}{l} \mathbf{g}(\mathbf{c}) - \mathbf{x} = \boldsymbol{\varepsilon} \\ \mathbf{f}_{MAL}(\mathbf{c}) = 0 \end{array} \right. \quad (6)$$

130 The differences of system (6) from the traditional speciation problem
 131 defined in (4) are the dimension of $\mathbf{g}$ and $\mathbf{x}$ ($\dim(\mathbf{g}) = \dim(\mathbf{x}) = N_d >$
 132 N_1) and errors in measurements $\boldsymbol{\varepsilon}$ which are included. $\boldsymbol{\varepsilon}$ can incorporate
 133 analytical errors in data, such as in data 1 to 4 in system (5), and uncertainty
 134 about the correct model, such as charge balance and equilibrium with calcite
 135 assumptions in system (5).

136 When solving speciation problems, it is common to use data equations
 137 which are either linear combinations of concentrations (e.g., *TIC*, alkalinity)
 138 or linear combinations of log-activities (e.g., equilibrium with minerals or
 139 gases). Moreover, the errors ($\boldsymbol{\varepsilon}$) of both types of data equations can have a
 140 normal or log-normal distribution. Therefore, the expressions of $\mathbf{g}(\mathbf{c})$ must
 141 be defined and calculated accordingly to the types of data equations (see
 142 Appendix A for details).

143 System (6) is overdetermined, therefore a non-linear least square fitting
 144 is required to minimize $\boldsymbol{\varepsilon}$, as described below.

145 2.3. Algorithm

146 We want to find the solution of (6) that minimizes the sum S of the
 147 weighted squares of the difference between measured and calculated data,
 148 defined as

$$S = \boldsymbol{\varepsilon}^t \mathbf{V}^{-1} \boldsymbol{\varepsilon} \quad (7)$$

149 where $\mathbf{V}$ is the covariance matrix ($N_d \times N_d$) of measurement errors. With-
 150 out loss of generality, we will assume errors to be not correlated, so that $\mathbf{V}$
 151 is a diagonal matrix, containing the variance of each i -th measurement, $\sigma_{e,i}^2$.

152 The condition leading to the minimum value of S is that its derivative with
 153 respect to the unknowns, $\ln \mathbf{c}_1$, is zero:

$$\frac{\partial S}{\partial \ln \mathbf{c}_1} = 2\boldsymbol{\varepsilon}^t \mathbf{V}^{-1} \frac{\partial \mathbf{g}}{\partial \ln \mathbf{c}_1} = 2\boldsymbol{\varepsilon}^t \mathbf{V}^{-1} \mathbf{J} = \mathbf{0} \quad (8)$$

154 where $\mathbf{J}$ is the jacobian matrix containing the derivatives of $\mathbf{g}(\mathbf{c})$ with
 155 respect to the unknowns, whose expression is derived and explained in Ap-
 156 pendix B. We decided to work with $\ln \mathbf{c}_1$ as variable but it would be equally
 157 possible to express all the equations as function of $\mathbf{c}_1$.

158 Approximating the function $\boldsymbol{\varepsilon}$ linearly between two sequential iterations
 159 k and $k + 1$

$$\boldsymbol{\varepsilon}^{k+1} = \boldsymbol{\varepsilon}^k + \mathbf{J}^k \Delta \ln \mathbf{c}_1^k \quad (9)$$

160 with

$$\Delta \ln \mathbf{c}_1^k = \ln \mathbf{c}_1^{k+1} - \ln \mathbf{c}_1^k \quad (10)$$

161 and substituting it in (8), the solution for a given iteration k is

$$\mathbf{J}^t \mathbf{V}^{-1} \mathbf{J} \Delta \ln \mathbf{c}_1 = -\mathbf{J}^t \mathbf{V}^{-1} \boldsymbol{\varepsilon} \quad (11)$$

162 After convergence, the covariance matrices of the estimation errors asso-
 163 ciated to $\ln \mathbf{c}_1$ ($\boldsymbol{\Sigma}_1$) and $\ln \mathbf{c}_2$ ($\boldsymbol{\Sigma}_2$) can be calculated. This can be useful to
 164 analyze the quality of the estimation (see section 2.4). $\boldsymbol{\Sigma}_1$ and $\boldsymbol{\Sigma}_2$, in fact,
 165 provide the uncertainty associated to the estimation of $\ln \mathbf{c}_1$ and $\ln \mathbf{c}_2$. $\boldsymbol{\Sigma}_1$
 166 ($N_1 \times N_1$) can be calculated by means of the "real" covariance matrix of the
 167 data, $\mathbf{C}_d$ ($N_d \times N_d$):

$$\Sigma_1 = Cov(\ln \mathbf{c}_1) = (\mathbf{J}^t \mathbf{C}_d^{-1} \mathbf{J})^{-1} \quad (12)$$

168 However, in reality $\mathbf{C}_d$ is not known. Therefore, it is necessary to make
 169 an hypothesis about its structure. A reasonable assumption defines $\mathbf{C}_d$ as
 170 proportional to S and to the covariance of measurement errors, $\mathbf{V}$:

$$\mathbf{C}_d = \sigma^2 \mathbf{V} \quad (13)$$

171 where $\sigma^2 = S/N_d$ (S was defined in equation 7). Substituting (13) into
 172 (12) we obtain

$$\Sigma_1 = \sigma^2 (\mathbf{J}^t \mathbf{V}^{-1} \mathbf{J})^{-1} \quad (14)$$

173 Σ_2 ($N_2 \times N_2$) can be calculated by taking into account the dependence
 174 of $\mathbf{c}_2$ on $\mathbf{c}_1$

$$\Sigma_2 = Cov(\ln \mathbf{c}_2) = \left(\frac{\partial \ln \mathbf{c}_2}{\partial \ln \mathbf{c}_1} \right) \Sigma_1 \left(\frac{\partial \ln \mathbf{c}_2}{\partial \ln \mathbf{c}_1} \right)^t \quad (15)$$

175 Details on the calculation of $(\partial \ln \mathbf{c}_2 / \partial \ln \mathbf{c}_1)$ are explained in Appendix
 176 B.

177 The steps of the proposed algorithm can be outlined as follows:

- 178 1. Set $\mathbf{x}$ and matrices of $\mathbf{g}(\mathbf{c})$ (see Appendix A)
- 179 2. Guess initial value of $\mathbf{c}_1^0$
- 180 3. Given $\mathbf{c}_1^k$, calculate secondary concentrations $\mathbf{c}_2^k = f(\mathbf{c}_1^k)$ and $\partial \mathbf{c}_2^k / \partial \mathbf{c}_1^k$
 181 from $\mathbf{f}_{MAL} = 0$ (see Appendix B)

- 182 4. Calculate $\boldsymbol{\varepsilon}^k$, Jacobian matrix $\mathbf{J}^k$, and RHS and LHS of system (11).
183 Solve system (11) and evaluate $\Delta \ln \mathbf{c}_1^k$
- 184 5. Update the solution $\ln \mathbf{c}_1^{k+1} = \ln \mathbf{c}_1^k + \Delta \ln \mathbf{c}_1^k$
- 185 6. Set $k=k+1$ and repeat steps 3. to 5. until convergence
- 186 7. After convergence, calculate $\boldsymbol{\Sigma}_1$ and $\boldsymbol{\Sigma}_2$

187 As convergence criteria, we check the maximum relative error between
188 two sequential iterations and the residual (RHS in system 11) at every it-
189 erations. The iterative process is stopped when both quantities are smaller
190 than threshold values defined by the user.

191 2.4. Testing approach

192 The algorithm was tested by means of two synthetic examples: first a
193 single reaction representing gypsum equilibrium at a temperature of 25 °C
194 in ideal conditions ($\mathbf{a} = \mathbf{c}$)

195 We chose arbitrarily a known solution of (16) and 5 possible measurements
196 with errors of $\log[Ca^{2+}]$ and $\log[SO_4^{2-}]$, decimal logarithm of calcium and
197 sulfate concentrations, respectively. Figure 1 shows the equilibrium line and
198 the exact solution of the speciation together with the 5 measurement points
199 that were used in this case. Both the traditional and the proposed methods
200 were applied to solve the speciation. Since the system is characterized by
201 one degree of freedom, i.e. one datum is necessary to solve the speciation,
202 first the traditional method was employed using only $\log[Ca^{2+}]$ data, and

203 later the proposed method was employed using both $\log[Ca^{2+}]$ and $\log[SO_4^{2-}]$
 204 measurements. The results were first compared in terms of logarithmic mean
 205 squared error, MSE_{log} :

$$MSE_{log} = \frac{1}{N} \frac{1}{N_s} \sum_{i=1}^N \sum_{j=1}^{N_s} \left[\log \left(\frac{c_{ij}}{c_j^*} \right) \right]^2 \quad (17)$$

206 where N is the number of measurements (5), N_s is the number of species
 207 (2), c_{ij} is the calculated concentration of the i -th measurement and j -th
 208 species, and c_j^* is the exact value of the j -th species. Comparing the two
 209 methods in terms of MSE_{log} was possible because the exact solution in this
 210 case is known. However, when a speciation is calculated using real data
 211 the exact solution is not known a priori. Therefore, we computed the co-
 212 variance matrices of estimation errors Σ_1 and Σ_2 defined in (14) and (15),
 213 respectively, and compared the estimation errors of the traditional and the
 214 proposed methods also in terms of the variable Var^* :

$$Var^* = \frac{1}{N} \frac{1}{N_s} \sum_{i=1}^N \left[\sum_{l=1}^{N_1} (\Sigma_{1, ll})_i + \sum_{m=1}^{N_2} (\Sigma_{2, mm})_i \right] \quad (18)$$

215 Var^* represents a mean value of the estimation errors variance of all the
 216 species. From (14) it can be noticed that Σ_1 depends on the error ε through
 217 the variable σ^2 . However, for the traditional speciation method $\varepsilon = 0$, hence
 218 $S = 0 \Rightarrow \sigma^2 = 0$ (see system 4). This makes (14) not suitable for the
 219 comparison. Therefore, we fixed $\sigma^2 = 1$ for the two methods. This way, we
 220 still guarantee that the real covariance matrix of data, $\mathbf{C}_d$ (see equation 13),
 221 is the same for both methods.

222 An input variable of the method is the variance of measurement errors

223 associated to the data, σ_e^2 (see equation 7). In this example we used the same
 224 value for both $\log[Ca^{2+}]$ and $\log[SO_4^{2-}]$ data ($\sigma_e = 0.17$), so that they have
 225 the same weight. In order to make the results of this example more general
 226 we tested again the two methods for 1500 measurements of $\log[Ca^{2+}]$ and
 227 $\log[SO_4^{2-}]$ with $\sigma_e = 0.17$. The exact solution was therefore perturbed 1500
 228 times by means of a lognormal distribution with standard deviation $\sigma_g = 0.17$
 229 to obtain the measurement points shown in figure 2. The use of a lognormal
 230 distribution allowed us to avoid possible negative values in concentrations in
 231 the measurements generation process.

232 The advantage of this simple problem is that it presents an analytical
 233 solution. In the case of using only $\log[Ca^{2+}]$ data, the variance of $\log[Ca^{2+}]$
 234 error will be σ_e^2 because $\log[Ca^{2+}]$ will remain unchanged. The same error
 235 will transfer to $\log[SO_4^{2-}] = \log K - \log[Ca^{2+}]$. Therefore, the expected value
 236 of Var^* is σ_e^2 . If both $\log[Ca^{2+}]$ and $\log[SO_4^{2-}]$ measurements are used, it
 237 is easy to check that minimizing $\varepsilon_{Ca^{2+}}^2 + \varepsilon_{SO_4^{2-}}^2$, where $\varepsilon_i = \log c_i - x_i$ ($i =$
 238 Ca^{2+}, SO_4^{2-}), subject to $\log[Ca^{2+}] + \log[SO_4^{2-}] = \log K$, leads to $\log[Ca^{2+}] =$
 239 $(\log K + x_{Ca^{2+}} - x_{SO_4^{2-}})/2$. Thus, the variance of both estimates is $\sigma_e^2/2$, which
 240 is the expected value of Var^* . This result will serve to test our approach and
 241 to illustrate the advantage of using redundant data.

242 As second example we chose the carbonate system defined in (1). The
 243 extended Debye-Hückell expression for activity coefficients was used in this
 244 example (Helgeson and Kirkham, 1974). As explained in section (2.1) the
 245 system is characterized by four degrees of freedom. We used as exact solution
 246 a water in equilibrium with calcite, with partial pressure of $CO_{2(g)}$ equal to
 247 $10^{-3.5}$, $a_{H_2O} = 1$ and electrically balanced. Its chemical composition is shown

248 in Table 1.

249 First we compared the traditional and the proposed methods to verify
250 the accuracy of the two algorithms in terms of speciation results. For this
251 purpose, six data were extracted from the exact solution to be used in the
252 speciation calculations (Table 2). The traditional speciation method was
253 employed using four data equations: *alkalinity*, Ca_{tot} , a_{H^+} and $a_{H_2O} = 1$.
254 Note that the proton activity presents a measurement error, therefore cannot
255 be eliminated. We will refer to this case as 'solution 1'. Afterwards we tested
256 the proposed method adding gradually redundant data to the previous three:
257 *TIC* ('solution 2'), activity of the gas, $a_{CO_2(g)}$ ('solution 3') and equilibrium
258 with calcite condition ('solution 4'). Afterwards we compared the solution
259 obtained with the traditional speciation method to the solutions obtained
260 using an increasing number of redundant data: from 1 in solution 2 to 3 in
261 solution 4. As for the gypsum example, we perturbed the data to generate
262 1500 possible measured values and then we compared the speciation results
263 in terms of MSE_{log} and Var^* , defined in (17) and (18), respectively.

264 The measured values were generated perturbing the logarithm of the ex-
265 act value (μ) with a standard deviation, σ_g , of 0.17 by means of a log-normal
266 distribution. The condition of calcite equilibrium was not perturbed ($\sigma_g = 0$),
267 since zero is the reference value of the saturation index for minerals in equi-
268 librium. The values of σ_g were used also to define the uncertainty associated
269 to every datum presenting analytical errors ($\sigma_e = 0.17$, see Table 2).

270 In reality, however, it is difficult to know the correct value of uncertainty
271 for each type of measurement. To analyze the effect of an incorrect measure-
272 ment error we performed a second group of simulations in which we changed

the σ_e values of all data one at a time and calculated MSE_{log} and Var^* as function of the standard deviation of measurement errors of every constraint. We chose two values of σ_e : the first larger than the one used to generate the perturbed measurements ($\sigma_e = 0.35 > \sigma_g$), to simulate a higher uncertainty associated to the data, and the second smaller ($\sigma_e = 0.09 < \sigma_g$), to simulate more certain data values.

3. Results

3.1. Gypsum example

Figure 3 shows the results of the traditional speciation method, i.e. using only $\log[Ca^{2+}]$ data. It can be noticed that the five points moved on the equilibrium line, since the equilibrium with gypsum was imposed as certain condition, along a line parallel to the y-axis which represents the imposed calcium concentration data. In this case $MSE_{log}=0.28$ and $Var^*=0.154$. Note that Var^* coincides with its expected value, σ_e^2 , once $\ln$ is converted to $\log_{10}$. Afterwards, the proposed method was tested, i.e., using both $\log[Ca^{2+}]$ and $\log[SO_4^{2-}]$ data. The results are shown in figure 4. It can be observed that while some of the points moved further from the exact solution with respect to the classical speciation results (white and black triangles), the others moved closer to the exact solution. However, for all the points the proposed algorithm minimizes the distance between measured and calculated data. The calculated mean squared error in this case was 0.23, smaller than 0.28 obtained with the traditional method. Moreover, $Var^*=0.077$, which coincides again with its expected value, $\sigma_e^2/2$.

The same methodology was employed to compare the two methods for

the 1500 measurement points of figure 2 and the resulting mean squared error decreased from 0.029 for the traditional method to 0.016 for the proposed methods. The value of Var^* also decreased by half, confirming its expected value: from 0.156 to 0.078 for traditional and proposed methods, respectively.

3.2. Carbonate example

The results of the comparison between the two methods in terms of MSE_{log} are shown in figure 5. It can be noticed that the value of the mean squared error for the traditional method (solution 1) is barely larger than 0.05, while it is smaller for the solutions using redundant data (solutions 2, 3 and 4). Moreover, increasing the number of redundant data used in the speciation contributes to reduce more the MSE_{log} value: it decreases from 0.04 using only one redundant data (solution 2) to 0.016 using 3 redundant data (solution 4).

Figure 6 shows the effect of changing the standard deviation associated to measurements (σ_e). Obviously its value does not affect solution 1, which is the result of a traditional speciation calculation. Neither does the value of σ_e for $a_{CO_2(g)}$ have an effect on solution 2 (figure 6e) because this solution does not use $a_{CO_2(g)}$ data. Nor does the σ_e for the assumption of equilibrium with calcite have an effect on solutions 2 and 3 (figure 6f), for the same reason. In general one can observe that the use of an incorrect standard deviation can worsen the solution with respect to the one obtained with the correct standard deviations. However, the quality of the solution in terms of MSE_{log} improves using redundant data with respect to the traditional speciation, despite a wrong choice about σ_e value. Decreasing the uncertainty relative to the equilibrium with calcite assumption (figure 6f) improves the

322 solution even with respect to the one obtained with correct σ_e values. This
 323 is because the correct value of σ_g for this datum is 0, not 0.17 (see Table 2).
 324 The effect of σ_e relative to alkalinity and TIC (figure 6c, d) are very similar
 325 as their values are very close, due to the fact that in this pH range the
 326 concentration of HCO_3^- is predominant with respect to carbonate species
 327 or OH^- concentrations. Finally, it seems that changing the uncertainty
 328 relative to Ca_{tot} (figure 6a) does not affect the solution. Nevertheless, when
 329 a large number of redundant data is used, such as in solution 4, the standard
 330 deviation seems to have a minor effect on the estimation error, MSE_{log} .

331 The effect of an incorrect value of σ_e on Var^* was also analyzed. Only the
 332 results for a_{H^+} and alkalinity are reported in figure 7 as the most representa-
 333 tive. It can be noticed that the error variance can be big for the traditional
 334 speciation method (solution 1), while it slightly decreases when redundant
 335 data are used (solutions 2, 3 and 4). Moreover, the more redundant data
 336 are used, the more the variance of estimation error decreases, converging to
 337 a value corresponding to the true standard deviation of measurement errors
 338 ($\sigma_e=0.17$).

339 4. Conclusions

340 We proposed a speciation algorithm that uses redundant data and acknowl-
 341 edges measurement errors, on the assumption that redundant data will reduce
 342 estimation errors in geochemical calculations.

343 We compared the proposed method with the traditional speciation method
 344 in terms of logarithmic mean squared error, MSE_{log} and mean value of es-
 345 timation error variance, Var^* . We tested both algorithms by means of two

346 synthetic examples. Both MSE_{log} and Var^* using redundant data are con-
 347 sistently smaller than in the traditional method.

348 The effect of measurement errors was examined in a carbonate system
 349 example. The algorithm is sensitive to the variance of measurement errors.
 350 Also, a wrong value of the standard deviation can worsen the results with
 351 respect to the ones obtained with the correct standard deviation. However,
 352 the effect of its value depends on the type of data associated to it. A wrong
 353 error associated to measurements can still improve the results in terms of
 354 mean squared error and variance of estimation error with respect to a tradi-
 355 tional speciation method, especially when a large number of redundant data
 356 are used.

357 Therefore we argue that the proposed method can improve the quality of
 358 the speciation results, reducing estimation errors.

359 **Appendix A. Error definitions**

360 The errors ϵ allowed in the proposed method can be additive or mul-
 361 tiplicative. Additive errors should lead to gaussian distributions, whereas
 362 multiplicative to lognormal distributions. Depending on the type of error,
 363 the function $\mathbf{g}(\mathbf{c})$ and the data $\mathbf{x}$ must be defined accordingly: arithmetic or
 364 logarithmic for additive and multiplicative errors, respectively.

365 Data used in speciation calculations are typically combinations of concen-
 366 trations or activity values. The former, which we name balance equations,
 367 are linear combinations of concentrations representing total concentrations,
 368 alkalinity, charge balance or *TIC* values. The latter are usually employed to
 369 fix pH values or to impose equilibrium with minerals or gases.

370 Distinguishing between these two types of data equations we can define:

$$\boldsymbol{\varepsilon} = \mathbf{B}\mathbf{c} - \mathbf{x} \quad (19)$$

371 for the balance equations and

$$\varepsilon_i = \prod_{n=1}^{N_s} a_n^{L_{in}} - x_i \quad (20)$$

372 for each i - th activity combination, respectively. $\mathbf{B}$ is a matrix of di-
 373 mension $(N_b \times N_s)$ and N_b is the number of balance equations. $\mathbf{B}$ contains
 374 different coefficients depending on the type of balance equation: ionic charge
 375 for charge neutrality, coefficients defining alkalinity or *TIC*, or component
 376 matrix elements for total concentration. $\mathbf{L}$ is a matrix of dimension $(N_a \times N_s)$
 377 containing the coefficients of the activity for every species involved in the
 378 combination. N_a is the number of activity conditions imposed.

379 If we want to use a log-distribution instead of a normal distribution of
 380 errors, one should use:

$$\boldsymbol{\varepsilon} = \ln(\mathbf{B}\mathbf{c}) - \ln \mathbf{x} \quad (21)$$

381 for the balance equations and

$$\boldsymbol{\varepsilon} = \mathbf{L} \ln \mathbf{a} - \ln \mathbf{x} \quad (22)$$

382 for the activity combinations, respectively.

383 Appendix B. Jacobian calculation

384 The jacobian, containining the derivatives of $\boldsymbol{\varepsilon}$ with respect to the state
 385 variables $\ln \mathbf{c}_1$ at every step of the iterative method, can be calculated as

$$\begin{aligned}
 \frac{\partial \varepsilon_i}{\partial \ln c_{1,j}} &= \frac{\partial \varepsilon_i}{\partial c_{1,j}} \cdot c_{1,j} \\
 &= B_{1,ij} \cdot c_{1,j} + \sum_{l=1}^{N_2} B_{2,il} \cdot \frac{\partial c_{2,l}}{\partial c_{1,j}} \cdot c_{1,j} \\
 i &= 1, \dots, N_b \\
 j &= 1, \dots, N_1
 \end{aligned} \tag{23}$$

386 from the definition (19) whereas by means of definition (21) results

$$\begin{aligned}
 \frac{\partial \varepsilon_i}{\partial \ln c_{1,j}} &= \frac{\partial \ln z_i}{\partial \ln c_{1,j}} \\
 &= \frac{1}{z_i} \cdot \frac{\partial z_i}{\partial \ln c_{1,j}} \\
 &= \frac{1}{z_i} \cdot \left(B_{1,ij} \cdot c_{1,j} + \sum_{l=1}^{N_2} B_{2,il} \cdot \frac{\partial c_{2,l}}{\partial c_{1,j}} \cdot c_{1,j} \right) \\
 i &= 1, \dots, N_b \\
 j &= 1, \dots, N_1
 \end{aligned} \tag{24}$$

387 being

$$z_i = \left(\sum_{m=1}^{N_1} B_{1,im} \cdot c_{1,m} + \sum_{l=1}^{N_2} B_{2,il} \cdot \frac{\partial c_{2,l}}{\partial c_{1,j}} \cdot c_{1,j} \right) \tag{25}$$

388 Matrices $\mathbf{B}_1$ and $\mathbf{B}_2$ are the parts of matrix $\mathbf{B}$ relative to primary and
 389 secondary species, respectively, and the derivatives of secondary concentra-
 390 tions with respect to primary concentrations can be calculated considering

391 that at every step of the iterative method the total derivative of $\mathbf{f}_{MAL}$ with
 392 respect to primary species concentrations is null:

$$\frac{d\mathbf{f}_{MAL}}{d\ln \mathbf{c}_1} = \frac{\partial \mathbf{f}_{MAL}}{\partial \ln \mathbf{c}_1} + \frac{\partial \mathbf{f}_{MAL}}{\partial \ln \mathbf{c}_2} \frac{\partial \ln \mathbf{c}_2}{\partial \ln \mathbf{c}_1} = 0 \quad (26)$$

393 Those derivative can be calculated by means of the following linear system

$$\frac{\partial \mathbf{f}_{MAL}}{\partial \ln \mathbf{c}_2} \frac{\partial \ln \mathbf{c}_2}{\partial \ln \mathbf{c}_1} = - \frac{\partial \mathbf{f}_{MAL}}{\partial \ln \mathbf{c}_1} \quad (27)$$

394 The conversion to $\partial \mathbf{c}_2 / \partial \mathbf{c}_1$ is straightforward, recalling that $d \ln x / dx =$
 395 $1/x$:

$$\frac{\partial c_{2,i}}{\partial c_{1,j}} = \frac{c_{2,i}}{c_{1,j}} \frac{\partial \ln c_{2,i}}{\partial \ln c_{1,j}} \quad (28)$$

396 The derivatives of (22), remembering the definition of activity ($\mathbf{a} = \boldsymbol{\gamma} \cdot \mathbf{c}$)
 397 and that $\boldsymbol{\gamma} = f(\mathbf{c})$, read

$$\begin{aligned} \frac{\partial \varepsilon_i}{\partial \ln c_{1,j}} &= L_{1,ij} + \sum_{m=1}^{N_1} L_{1,im} \frac{\partial \ln \gamma_{1,mj}}{\partial \ln c_{1,j}} + \\ &+ \sum_{l=1}^{N_2} L_{2,il} \left(\frac{\partial \ln \gamma_{2,lj}}{\partial \ln c_{1,j}} + \frac{\partial \ln c_{2,lj}}{\partial \ln c_{1,j}} \right) \end{aligned} \quad (29)$$

$$i = 1, \dots, N_a$$

$$j = 1, \dots, N_1$$

398 Matrices $\mathbf{L}_1$ and $\mathbf{L}_2$ are the parts of matrix $\mathbf{L}$ relative to primary and
 399 secondary species, respectively.

400 The derivatives of (20) with respect to the state variables can be calcu-
 401 lated from

$$\begin{aligned}
\frac{\partial \varepsilon_i}{\partial \ln c_{1,j}} &= \prod_{n=1}^{N_s} a_n^{L_{in}} \cdot \left[L_{1,ij} + \sum_{m=1}^{N_1} L_{1,im} \frac{\partial \ln \gamma_{1,mj}}{\partial \ln c_{1,j}} + \sum_{l=1}^{N_2} L_{2,il} \left(\frac{\partial \ln \gamma_{2,lj}}{\partial \ln c_{1,j}} + \frac{\partial \ln c_{2,lj}}{\partial \ln c_{1,j}} \right) \right] \\
i &= 1, \dots, N_a \\
j &= 1, \dots, N_1
\end{aligned}
\tag{30}$$

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Figure 1: Five measurements, exact solution and equilibrium line for gypsum example.

Figure 2: 1500 measurement points generated by means of a lognormal distribution for gypsum example.

Figure 3: Speciation results of traditional speciation method, exact solution and equilibrium line for gypsum example. Dashed arrows show the movement of the five points from initial conditions, represented with stars.

Figure 4: Speciation results of proposed method, exact solution and equilibrium line for gypsum example. Dashed arrows show the movement of the five points from initial conditions, represented with stars.

Figure 5: MSE_{log} for traditional speciation method (solution 1) and proposed method (solutions 2, 3 and 4) obtained with σ_e values of table 2.

Figure 6: MSE_{log} obtained changing values of σ_e of each data: (a) Ca_{tot} ; (b) a_{H^+} ; (c) alkalinity; (d) TIC ; (e) $a_{CO_{2(g)}}$; (f) calcite equilibrium.

Figure 7: Var^* obtained for different values of σ_e of (a) a_{H^+} and (b) alkalinity.

Table 1: Exact solution for carbonate example.

	Species	Values
c^*	Ca^{2+}	$4.92 \cdot 10^{-4}$
$[mol/l]$	H^+	$5.51 \cdot 10^{-9}$
	HCO_3^-	$9.63 \cdot 10^{-4}$
	$CO_{2(aq)}$	$1.07 \cdot 10^{-5}$
	CO_3^{2-}	$9.78 \cdot 10^{-6}$
	OH^-	$2.01 \cdot 10^{-6}$
a^*	$CO_{2(g)}$	$3.16 \cdot 10^{-4}$
$[bar]$		
SI	<i>Calcite</i>	0.0
(Sat. Index)		

Table 2: Mean values and standard deviations adopted to generate 1500 realizations of data for the carbonate example.

Data	μ	σ_g	σ_e	ε equation
Ca_{tot}	$4.92 \cdot 10^{-4}$	0.17	0.17	(21)
a_{H^+}	$5.29 \cdot 10^{-9}$	0.17	0.17	(22)
Alkalinity	$9.85 \cdot 10^{-4}$	0.17	0.17	(21)
TIC	$9.84 \cdot 10^{-4}$	0.17	0.17	(21)
$a_{CO_{2(g)}}$	$3.16 \cdot 10^{-4}$	0.17	0.17	(22)
Calcite Eq.	0	0	0.17	(22)

Units are in *mol/l* except for $a_{CO_{2(g)}}$ which is expressed in *bar*.