Comment

A foray into false positive results in mineral dissolution and precipitation studies

D. Wolff-Boenisch a,*, I.M. Galezcka b, K.G. Mesfin b, S.R. Gislason b

a Department of Applied Geology, Curtin University, GPO Box U1987, Perth, 6845, Western Australia, Australia
b Institute of Earth Sciences, University of Iceland, Sturlugata 7101, Reykjavik, Iceland

ABSTRACT

This study presents and discusses several case studies of false positive results in mineral/rock dissolution and precipitation studies and the lessons that can be learned from them.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Studies on the kinetics of mineral and rock dissolution are vital for our understanding of element cycles, whether in natural or man-made settings. It is therefore no surprise that with respect to the matrix of dissolution experiments there has been virtually no mineral untouched and no stone unturned in the last decades to refine our empirical view of matter fluxes derived from reactor experiments. The rate laws that govern the dissolution of these matrices and which have been inferred from these experimental studies1 have entered multiple reaction path and/or reactive transport models to anticipate their corrosion resistance and stability over time. The pertinent literature1 is full of examples of such experimentally derived kinetic rate expressions that, once implemented in codes, have increased substantially the prognostic value of the calculation. Reading the bulk of these publications, the reader comes generally away with the impression that mineral dissolution/precipitation experiments are straightforward and without hitch; and that it is the subsequent data interpretation and rate creation that is difficult and challenging. This contribution seeks to relativise this impression by providing three fundamentally different case studies that illustrate the potential pitfalls that especially novice experimenters may encounter during dissolution studies in batch or flow-through reactors. It is the kind of negative information that never makes it into publications, perhaps because it is indeed never experienced or, more likely, because a false-positive result is either picked up on time to be deleted from the text or not realised and hence misinterpreted—to the present day.

1.1. Case: the matrix

1.1.1. Part 1

The first example of a false-positive event stems from a set of kinetics experiments on albite. The aim was to elucidate albite’s dissolution behaviour in the presence of different cations and ionic strengths at low pH and ambient temperature (pH 3.5 and 25 °C). The set-up used to carry out the experiments is described in more detail in Stockmann et al. (2011) and consists of a custom made 300 ml Teflon flow-through reactor with a floating stir bar and a heating and stirring plate. A certain amount of albite was ground, sieved to a specific grain size fraction, washed several times with acetone to remove ultra-fines, dried, weighed and inserted into the reactor and dissolved over one month’s time in an electrolyte of specific ionic strength and composition (10 mM NaCl for set A and 10 mM KCl for set B). The major electrolyte cation was then replaced with a divalent one (10 mM CaCl2 for set A and 10 mM MgCl2 for set B) and the albite further dissolved for another month in the same reactor. Table 1 compiles the most important parameters of this experimental set whereas Fig. 1 shows the key findings. As customary in silicate dissolution studies, the elemental concentrations of the major network-forming ions (Si and Al) are plotted as a function of time and display that albite steady-state rates under similar experimental conditions have been reported in the literature (Chou and Wollast, 1984; Gudbrandsson et al., 2014; Hellmann, 1995; Knauss and Wolery, 1984).

* Corresponding author.
E-mail address: Dominik.Wolff-Boenisch@curtin.edu.au (D. Wolff-Boenisch).
1 Given the vast literature on this subject, the authors refrained from singling out any particular work, study or compilation and kept this paragraph deliberately void of references.
but were performed for shorter time intervals in the range of days or few weeks so this observation of persistent non-steady-state after this relatively long experimental duration of one and two months, respectively was unexpected -as was the fact of non-stoichiometry of the albite dissolution reaction which was invariably highly incongruent with respect to Al (Fig. 2). Incongruent mineral dissolution is often observed in the initial phase of dissolution experiments and can by no means be alleged as a reason for a spurious experiment but in the case of (sodium rich) feldspars dissolving at low pH, literature does suggest the attainment of stoichiometric dissolution (Stillings and Brantley, 1995). Rather than non-steady-state or non-stoichiometry of albite dissolution, it was the unusually high Si outlet concentration that prompted us to look for a contamination source in our experiments. While the Si concentration decreased with time there were time spans where it stayed constant for a while. It was during those times that averaged pseudo-steady-state Si rates were determined and compared to literature release rates from albite dissolution at similar pH/T conditions. While such a comparison is inconsistent as ours were not true but ‘transitional steady-state conditions’, it nevertheless revealed that the Si release rates of this study were at least 1–1.5 orders of magnitude larger than the fastest albite rates that were retrieved from the literature. A routine X-ray diffraction (XRD)

### Table 1

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>NaCl, 10</td>
<td>25</td>
<td>3.7–3.8</td>
<td>0.8</td>
<td>45–125</td>
<td>668</td>
</tr>
<tr>
<td></td>
<td>CaCl₂, 10</td>
<td>25</td>
<td>3.7–3.8</td>
<td>0.8</td>
<td>45–125</td>
<td>668</td>
</tr>
<tr>
<td>B</td>
<td>KCl, 10</td>
<td>25</td>
<td>3.7–3.8</td>
<td>0.8</td>
<td>45–125</td>
<td>668</td>
</tr>
<tr>
<td></td>
<td>MgCl₂, 10</td>
<td>25</td>
<td>3.7–3.8</td>
<td>0.8</td>
<td>45–125</td>
<td>646</td>
</tr>
</tbody>
</table>

Fig. 1. The elemental release of Si (a, c) and Al (b, d) from the experimental sets A (a, b) and B (c, d).

Fig. 2. Al/Si stoichiometry of the albite dissolution in experimental set A (a) and B (b), based on a structural Al/Si of albite (0.44) derived from X-ray fluorescence analysis.
analysis check, which was performed initially on the commercially acquired albite material, revealed only albite (Fig. 3) but energy-dispersive X-ray analysis in conjunction with scanning electron microscopy (SEM-EDX) confirmed the presence of nepheline. Since the mm large grains initially bought as albite had been ground to a fine powder, it is impossible to say if the nepheline contamination went back to just a few grains of pure nepheline or if the albite grains themselves were nepheline bearing because they were sourced from very alkaline rocks such as syenites, phonolites or tephrites. So we had been dissolving nepheline-laced albite - but could that little nepheline (<3%) have such an impact on the rates as to basically mask albite dissolution?

The answer is given in Fig. 4, which illustrates the stoichiometry of the dissolution experiments again, this time however based on the structural AI/Si ratio of nepheline (0.94) instead of albite (0.44) that was used for initial stoichiometry calculations (Fig. 2). Note that as Na and K were either major electrolyte ions or potential contaminations in the other electrolyte solutions (NaCl, KCl, CaCl₂, and MgCl₂), they were not used in the stoichiometry discussion.

Fig. 4 indicates that over the entire experimental duration nepheline is the primary source for the Al concentration in solution whereas the Al contribution from albite is too weak to create a degree of non-stoichiometric preferential release. A nepheline rate comparison of our pseudo steady-state rates (between 10⁻⁸.5 and 10⁻⁹.0 mol/m²/s, depending on the electrolyte cation) and a literature value of 10⁻⁸.9 mol/m²/s for annealed pure nepheline glass at pH 4 and 25 °C (Hamilton et al., 2001) substantiates the assumption of overriding nepheline dissolution in our experiments. This is not surprising after all as nepheline dissolves 15 orders of magnitude faster than albite under acidic conditions (Hamilton et al., 2001). Thus, as long as there is nepheline in the matrix, its dissolution masks any contribution from albite. Over time, this minor phase will be removed quantitatively but reactor experiments routinely run for days or weeks, at best months and that may not be long enough for this chemical removal to be of consequences as our case study shows. This phenomenon that the dissolution of an accessory phase can predominate the solution chemistry is known from weathering studies in large and small catchment areas (e.g. Himalayas and Alaska) where disseminated calcite, occupying less than 1/5 of the entire silicate bedrock lithology (and in some instances only around 1%), accounted for the primary alkalinity and watershed chemical composition (Jacobson and Blum, 2000; Skidmore et al., 2005; White et al., 1999; Wolff-Boenisch et al., 2009). This predominance is possible because calcite dissolves orders of magnitude faster than silicate minerals. Gislason and Oelkers (2011) compiled the dissolution rates of some salt, carbonate and silicate phases as a function of pH (Fig. 5), illustrating the large difference in dissolution kinetics that exists between salt and carbonate versus silicate phases, which is even more accentuated for felsic silicates such as albite. The implications are to complement XRD (including Rietveld refinement as this technique is only sensitive to mineral abundances of ≥2%) with SEM-EDX or better still electron microprobe as primary characterisation tool for the starting material. This is especially recommended for feldspar solid-solutions, where the solution chemistry and thus dissolution rates may very well go back to the hydrolysis of different feldspar phases or compositions that are the product of exsolution, zoning, twinning, or intergrowth during the mineralisation process. A more rigorous material characterisation approach will also ensure to pick up contamination of accessory phases whose dissolution kinetics may be fast enough compared to the target phase to contribute a major false positive signal to elemental release rates.

1.1.2. Part 2

The second example where experimenters take erroneously the sample integrity for granted is in the grain size range used for the dissolution studies. Sieves are routinely deployed to cull the desired size fraction which is then duly reported in the publications. But how efficient is this approach and how accurate are the results? Is the grain size really between those stipulated mesh sizes and what if it is not? Will there be any consequences of determining and/or reporting erroneous grain sizes or no grain sizes at all? After all, grain sizes should not interfere with dissolution kinetics and rate determinations or expressions; that is why rates are normalised to their specific surface area in the first place. Because our group has been working extensively on the dissolution of different basalt batches from the same locality in Iceland (so-called Stapafell basalt which is chemically a mid-ocean ridge basalt), we set out to investigate in how far sample preparation and cleaning were related to reported and genuine grain sizes and measured specific surface area, according to the Brunauer, Emmett, and Teller theory (BET). We had three different reference materials to our disposition that had been well characterised in the past, including SEM micrographs and BET measurements:

a) Stapafell glass used in the publication of Oelkers and Gislason (2001) and Gislason and Oelkers (2003); labelled G_old
b) Stapafell glass used in the publication of Stockmann et al. (2011) and Wolff-Boenisch et al. (2011); labelled G_fair
c) Stapafell glass used in the publication of Galeczka et al. (2013, 2014); labelled G_new

Table 2 summarises the pertinent information on these three rock batches. Although G_old and G_fair stem from the same outcrop and were, by and large, treated in the same fashion (crushed ‘gently’ with a rubber coated hammer, sieved manually, washed with acetone), G_old’s BET surface area was nearly four times larger. To rule out that an error in the old sample treatment protocol had caused such high BET, a fresh sample from the G_old stash was taken and the BET surface area re-measured. It yielded initially an even larger specific surface area of 2.7 m²/g, 15% higher than the original value of 2.3 m²/g. However, after thorough cleaning of the glass with deionised water in a vat and siphoning off the fine particles according to Stoke’s law (cf. Table 3), the cleaned sample of G_old was reduced to 2.2 m²/g, validating thus its original BET. The comparatively low BET of G_fair did not fit in, all the more because G_new, a Stapafell variety that was taken some distance away from the original Stapafell supply, yielded again a fairly large BET of 2.2 m²/g. Because the latter had only been cleaned with DI water after Stoke’s Law, a sub-sample was subjected to repeated acetone cleaning cycles to see if this could decrease the BET to the level of G_fair. However, it yielded a new BET of 1.9 m²/g, again validating the original value. Because G_old and G_new displayed

![Fig. 3. X-ray powder diffraction analysis of the starting material used for the albite dissolution experiments. All major and minor peaks are consistent with those of albite.](image-url)
similar, representative but relatively high BET surfaces using different crushing, sieving, and cleaning techniques, contributions from these techniques to the large BET was ruled out. Hence, grain size distribution (GSD) analysis on the three glass varieties was carried out to determine if this could explain the inconsistencies in the BET values. Fig. 6 displays the three grain size distributions for G_old, G_fair, and G_new, respectively. It was surprising to find that only ca. 55% of the grains distributed themselves over the nominal grain size range of 45–125 μm (or 45–100 μm in the case of G_new). All glasses had quite a large percentage between 30 and 40% above 100 or 125 μm, whereas the percentage of material below the 45 μm mark was 6%, 15%, and 12% for G_old, G_fair, and G_new, respectively. It means that the glass with the largest BET (G_old) had the lowest percentage of small particles whereas the glass with the lowest BET (G_fair) had the highest percentage of small particles. This seems counterintuitive. Given that G_old and G_fair powders were prepared in the same way, the conclusion is that G_fair must be very smooth to avoid the relative over-abundance of fine particles to contribute to its low BET. This assumption was corroborated by SEM analysis that found invariably smooth glass surfaces. Furthermore, G_old cannot derive its large BET from the little percentage of small particles; it is likely caused by genuine surface roughness, i.e. porous surfaces and/or coatings but corroborating this point proved elusive. The same applies to G_new; SEM revealed consistently smooth surfaces, like in the case of G_fair, so its high BET can still not be explained satisfactorily other than by postulating some undetected surface roughness. Admittedly, G_new was treated with a Jaw crusher and shaken automatically compared to their counterparts but neither GSD nor SEM analyses indicate this had a particular effect. Moreover, the

**Fig. 4.** Al/Si stoichiometry of the albite dissolution in experimental set A (a) and B (b), based on a structural Al/Si of nepheline (0.94) derived from X-ray fluorescence analysis.

**Fig. 5.** Dissolution rate of salts, minerals and basaltic glass at 25°C as a function of pH. Modified after Gislason and Oelkers (2011).

### Table 2

Data on cleaning techniques, BET and grain size distribution of the three Stapafell glass sets used in this study.

<table>
<thead>
<tr>
<th>Study</th>
<th>BET m&lt;sup&gt;2&lt;/sup&gt;/g</th>
<th>GSD&lt;sup&gt;a&lt;/sup&gt; Nominal</th>
<th>GSD&lt;sup&gt;a&lt;/sup&gt; Measured</th>
<th>≤ 45 μm %</th>
<th>≥ 100/125 μm %</th>
<th>d&lt;sub&gt;eff&lt;/sub&gt; μm</th>
<th>Crushing&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Sieving&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Cleaning&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>G_old</td>
<td>2.3/2.2</td>
<td>45–125</td>
<td>18–246</td>
<td>6</td>
<td>41</td>
<td>87</td>
<td>Hand</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>G_fair</td>
<td>0.6</td>
<td>45–125</td>
<td>6–246</td>
<td>15</td>
<td>30</td>
<td>65</td>
<td>Hand</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>G_new</td>
<td>2.2/1.9</td>
<td>45–100</td>
<td>18–206</td>
<td>12</td>
<td>35</td>
<td>77</td>
<td>Hand</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

<sup>a</sup> Where more than one value is given, the 2nd value refers to a repeated measurement after additional cleaning, see text for more explanation.

<sup>b</sup> Grain size distribution; the measured range encompasses 98% of the grains.

<sup>c</sup> This is the percentage of grains that were either below or above the nominal particle size.

<sup>d</sup> d<sub>eff</sub> is the effective particle diameter and determined by (d<sub>max</sub>–d<sub>min</sub>)/ln(d<sub>max</sub>/d<sub>min</sub>) (Tester et al., 1994).

<sup>e</sup> Material crushing with a plastic hammer is deemed more gentle than with a jaw crusher producing less ultrafine particles.

<sup>f</sup> The vibrations of a sieve shaker are considered more effective than hand shaking in sorting the grains into their respective size fractions.

<sup>g</sup> ‘Stoke’ means mixing the sieved particles of desired grain size range with DI water in a vat and create a suspension by vigorous stirring. After a specific time, determined by Stoke’s law, the supernatant is siphoned off, taking the remaining unwanted fine particles with it while the target grain size (and larger particles) settle. It corresponds to a washing cycle with deionised water. ‘Acetone’ means rinsing the sieved and pre-washed particles with acetone in a beaker. This can be done manually by shaking the suspension with a glass rod or in an ultrasonic bath. Usually several acetone cycles are applied to ensure no ultra-fines are still sticking to the particle surface.

### Table 3

Experimental parameters for the basaltic glass (G) and crystalline basalt (X) dissolution study, respectively.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass (G)</td>
<td>NH₄CO₃, 40</td>
<td>90</td>
<td>-6</td>
<td>0.2</td>
<td>45–100</td>
<td>1176</td>
</tr>
<tr>
<td>Crystalline (X)</td>
<td>NH₄CO₃, 40</td>
<td>90</td>
<td>-6</td>
<td>0.2</td>
<td>45–125</td>
<td>1176</td>
</tr>
</tbody>
</table>
methods (all the featured false positives and is rather meant to promote GSD \(50/C14\)). This larger grain size range, albeit marginally in this study. The deff See text for more explanation and references.

ruling out any significant effect on the GSD. The GSD analysis is instrumental in area of the material, at least not for glasses. The two different sieving each other and do no exert any apparent effect on the BET surface area of the material, at least not for glasses. The two different sieving methods are comparable to each other and do no exert any apparent effect on the BET surface area of the material, at least not for glasses. The two different sieving methods are comparable to each other and do no exert any apparent effect on the GSD. The GSD analysis is instrumental in ruling out any significant contribution from fine particles to the BET. It is therefore a diagnostic tool to complement SEM analysis in search for surface roughness that may be indicated by BET analysis. Equally important, GSD analysis is essential to establish the effective grain size range which turned to be much larger than according to the nominal sieve sizes in this study. A staggering 45% of the grains lay outside the brackets; this is yet another example of a false positive signal because there is a considerable amount of grains outside the expected range that will contribute to the overall matrix dissolution and elemental release while not being recognised. In how far this expanded particle size range affects the rate measurably is debatable; after all the ‘new’ particles’ presence is implicit in the BET, although unbeknownst to the experimenter. The geometric surface area, however, which is calculated based on the effective particle diameter \(d_{\text{eff}}\) (cf. Table 3) is indeed affected by this larger grain size range, albeit marginally in this study. The \(d_{\text{eff}}\) for the nominal range is 78 \(\mu\)m while it varies from 65 to 87 \(\mu\)m for the three glass batches. This example is the least consequential of all the featured false positives and is rather meant to promote GSD analysis as diagnostic tool to corroborate that cleaning has been thorough and to determine in how far high BET values are related to surface roughness or (very) small particles. While SEM can achieve similar tasks (and should be used to establish the solid’s chemical composition), it requires more time and thus money for a full characterisation and may still not guarantee to find those rough particles or micro-fines that did alter the BET; that is what happened during the SEM analysis of \(G_{\text{new}}\). Last but not least, GSD analysis raises the question of the motivation and purpose of reporting grain size ranges in the first place. What is its meaning, especially when finding that close to half of the particles have not been accounted for?

### 1.2. Case: the reactor

Yet another example that involves false positives is the reactor material. Needless to say that the experimenter needs to be sure that the solution chemistry is a true reflection of the dissolution and precipitation process in order to extract rates and rate expressions representative of the actual process. Hence, the experimenter has to ensure that the reactor material does not contribute to the solute signal. The choice of reactor and reactor peripheral material (valves, gauge, stirrer, lid, tubing, back pressure regulator) is challenging and ranges from pure Teflon and titanium over alloy types such as Hastelloy, Monel, Inconel to the standard 316 stainless steel. Budget restrictions together with the nature of the working solution (highly corrosive/volatile, high ionic strength) will influence the decision. In this case study, a flow-through experiment was designed to look at seawater-basalt interactions at circum-neutral pH and high temperature. Aim was to study the secondary phases that would form after injection of \(\text{CO}_2\)-saturated saline solution into deep basalt formation and neutralisation of the initially acid carbonated water during reaction with the basic rock (Siggusson et al., 2015; Wolff-Boenisch et al., 2011).

Table 3 summarises the main aspects of this experimental set. The reactor was a Titanium Part\(^\text{TM}\) reactor, where most wet parts were made of grade2 Ti, with the exception of the needle/check valves, that were made of Monel400 alloy. The Ti needle valves turned out to be a laboratory hazard for pressure work because the soft Ti metal stem was chafing off during repeated opening/closing actions until no stem was there to actually close the reactor valve \(\text{another bit of vital information that is usually omitted in papers, i.e. talking about equipment failure}.\) The Monel400 has excellent corrosion resistance in a range of media, including sea water, hydrofluoric and sulfuric acid and alkalies, and is widely used for marine engineering applications (www.specialmetals.com/special-metals-nickel-alloy-handbook). Given the planned experiments of (ultra)mafic rock seawater interactions (W Wolff-Boenisch et al., 2011), Monel400 was thus chosen for the valves rather than Ti, being equally corrosion resistant. The experiments ran for 49 days.

Table 4

<table>
<thead>
<tr>
<th>Experiment</th>
<th>T/pH</th>
<th>Rate(_{\text{geom}}) [mol/cm(^2)/s]</th>
<th>Mass [g]</th>
<th>Time [s]</th>
<th>SA(_{\text{geo}}) [cm(^2)/g]</th>
<th>Amount [moles]</th>
</tr>
</thead>
<tbody>
<tr>
<td>forsterite</td>
<td>90/3.0</td>
<td>4.78e-10</td>
<td>2</td>
<td>86,400</td>
<td>145</td>
<td>1.2e-02</td>
</tr>
<tr>
<td>basalt</td>
<td>50/3.1</td>
<td>4.97e-12</td>
<td>2</td>
<td>86,400</td>
<td>246</td>
<td>2.1e-04</td>
</tr>
</tbody>
</table>

a The BET rate for the forsterite \(10^{-12.76}\) was taken from Hänchen et al. (2006) and multiplied by the reported roughness factor \(5.5\) to yield the geometric rate at 90 °C and pH3.0. The BET rate for the basalt \(10^{-9.66}\) was taken from Gudbrandsson et al. (2014) and multiplied by the reported roughness factor \(28.6\) to yield the geometric rate at 50 °C and pH3.1.

b The masses for basalt and forsterite were those used by Gudbrandsson et al. (2014) and Pokrovsky and Schott (2000).

c The duration of the experiments was assumed to be 24 h, in accordance with Gudbrandsson et al. (2014) and Pokrovsky and Schott (2000), respectively.

d The geometric surface areas stem from Gudbrandsson et al. (2014) and Hänchen et al. (2006), respectively.

e Moles are calculated by multiplying the previous four columns. This is the amount expected to dissolve from the matrix under steady-state far-from-equilibrium conditions after the elapsed time.

---

**Table 4**

Data from batch dissolution experiments on forsterite and basalt from the literature indicate the moles of dissolved material that can be expected after attainment of steady-state.

---

**Fig. 6.** Grain size distribution (GSD) analysis of the three different basaltic glass batches (\(G_{\text{old}}, G_{\text{fair}}, G_{\text{new}}\)) that have been used for dissolution studies in the literature. The vertical lines represent the nominal particle size limits derived from sieving (45, 100, 125 \(\mu\)m). Below and above those limits there ought to be no particles. See text for more explanation and references.
under very low flowrates to enable long residence times in the two reactors. That was intended to emulate pore conditions where carbonate precipitation is anticipated to take place that binds CO₂. The solute chemistry was monitored during that time as well as solid samples taken after the experiments finished looking at the secondary phases that had formed. The SEM-EDX was implemented to screen the solids for areas of high precipitation that would need further scrutiny with electron microprobe. Large was our surprise when we found ample evidence of NiO phases that had precipitated in both reactors. Fig. 7 displays how some basalt grains had been entirely covered with this Ni varnish whereas in other parts this cover had chipped off revealing the smooth surface (in this case of glass) underneath.

Besides a strong Ni signal from SEM-EDX, the spectra also revealed that the coating was either very thin or porous as the alumino-silicate character of the underlying basalt still came through in the EDX spectra. Looking closer at the Ni solute chemistry from the reactor outlets -an element that is routinely deemed irrelevant in our experiments (and in the blank that preceded the experiments), confirmed a staggering contribution from this ‘trace' element to the solution chemistry. Fig. 8 compiles the Ni solute concentrations that composed 50% and 40% of the entire TDS (bar contributions from the inlet) in the basaltic glass and crystalline basalt experiments, respectively.

Part of the solute Ni had apparently been incorporated into unwanted and not representative secondary phases, also indicated by its decreasing solute concentration over time. And although no other secondary phases were unambiguously detected by SEM-EDX (e.g. zeolites, clays, carbonates), and although the solution chemistry indicated stoichiometry at least of the glass dissolution with no loss of major solutes (except for Fe) into secondary silicate and carbonate phases, it cannot be ruled out that the secondary NiO may have served as surface template for heterogeneous nucleation of minute amounts of other secondary phases, minuscule enough...
to evade being picked up by the solution chemistry and/or SEM. This example is not so much about a false positive in the sense that it generates a signal (substantial solute Ni and solid NiO) where none is expected because the experimenter can easily pick it up with the right analytical tools. Rather, secondary metal-oxide phases from contaminating reactor material may act as catalysts and promote subsequent heterogeneous nucleation of secondary silicate/carbonate phases that otherwise may not precipitate—or at least not to such degree. Consequently, the interpretation of the results may be flawed and erroneous conclusions may be drawn and that is the problem of this kind of false-positives.

1.3. Case: the protocol

This last part is the trickiest to describe and evaluate because no own experimental studies are available that can be displayed to make a case for a false positive. As such this chapter relies on observations extracted from third party publications without directly referencing them, for obvious reasons. This false-positive example revolves around the hitherto unquestioned formation of secondary phases out of saturated solutions, especially in a batch reactor. Are these formations genuine or partially artefacts of the change in reaction conditions during the experiment? As such, the discussion here pertains to the protocol that is applied to high P/T experiments on water-rock interactions and is especially true for dissolution/pre-incipitation studies under elevated pCO2 pressure in the presence of Ca,Mg-rich rocks/minerals to study the potential for carbonate formation. Pressurising the batch reactor with CO2 lowers the pH sufficiently to create acidic conditions; depending on the pCO2 and the buffer capacity of the inlet/inital solution, the in situ pH varies usually between 3 and 3.5. Under these pH conditions, the alkalinity is so low that a lot of divalent cations from the matrix are required to reach carbonate saturation. Raising the temperature in the reactor will decrease carbonate solubility to reach more favourable precipitation conditions—and effectively, many published papers on the subject of water-(ultra)mafic rock/mineral interactions under elevated pCO2 and high/er temperatures report invariably copious/pervasive precipitation of carbonates from the solution which is attributed to readily available divalent cations and fast dissolution kinetics of the matrix. However, none of these papers treat in more theoretical detail how it was possible to raise the pH via dissolution of the basic matrix to a degree of sustained carbonate formation. With every mole of dissolving material and mole of consumed protons, the alkalinity rises proportionally in solution and creates a formidable buffer; it is by no means clear that the dissolution process is able to overcome this buffer. In fact, theoretical calculations and modelling indicate that the solution will reach the steep slope of a ‘buffer hill’ that needs to be overcome by continuous large scale rock/mineral dissolution to reach and maintain carbonate saturation (Wolff-Boenisch, 2011). Another, evidently never discussed alternative way of explaining the formation of carbonates is the substantial increase in saturation that cannot be eluded by going from the experimental conditions (high pCO2 and T) to ambient lab conditions when terminating the experiments. Controlled depressurisation of the reactor is not instantaneous and usually takes several hours, while the temperature is slowly brought down. During this time lapse, the carbonate saturation increases substantially when the dissolved CO2 degasses and reverts the process of carbonic acid formation, increasing the pH in a more efficient and faster way than by mineral dissolution.

To back this crucial point, batch dissolution calculations were carried out with PHREEQC3 (Parkhurst and Appelo, 2013). The basic model consists of carbonating pure water at a pCO2 of 100 bar and temperatures of 50, 75, and 100 °C and subsequently dissolving forsterite and basalt, respectively to reach magnesite or calcite saturation. The assumptions underlying this model have been summarised in Table 3, which compiles the key parameters that were used to estimate the moles of matrix that dissolve under the prescribed pCO2 and T conditions. Based on far-from-equilibrium dissolution rates from the literature, it is anticipated that after one day of dissolution at 90 °C and pH 3, the batch solution will contain 10 mmoles of forsterite. This is the amount that was successfully dissolved via PHREEQC3 to equilibrate with the previously carbonated solution.

Fig. 9 shows the result for the forsterite dissolution model. Carbonating pure water at a pCO2 of 100 bar creates an initially acidic solution whose protons attack the forsterite surface. The progressive dissolution of forsterite and release of Mg consumes the protons and the solution approaches magnesite saturation. PHREEQC3 was used to model the batch reactor experiment which was stopped after 10 mmoles of forsterite dissolved at different temperatures (dotted lines, capped by a black square). As can be seen, the solution has become slightly supersaturated with magnesite only at the highest temperature, whereas at 50° and 75 °C the system has not or only barely reached saturation, respectively. As magnesite precipitation requires a relatively large degree of supersaturation (>1, Saldi et al., 2009), stopping the experiment here will not suffice to prompt, let alone maintain magnesite precipitation. However, if such a batch reactor experiment was terminated, the ensuing degassing during cooling would drive this system into considerable magnesite supersaturation (solid curves in Fig. 9). The retrograde solubility of carbonates and increased CO2 solubility at lower temperatures mitigate the rise in magnesite saturation during degassing and cooling. This retrograde T effect is most accentuated at the highest modelled T of 100 °C, whose curve falls temporarily back towards saturation before reaching the highest degree of supersaturation. Under the modelled conditions, CO2 degassing has an overall larger impact on carbonate saturation compared to cooling. Given that the system approaches equilibrium in a batch reactor, which slows down and finally arrests the dissolution, the assumptions in Table 3, especially those referring to the maintenance of a steady-state rate for 24 h are already at the upper limit of what might be expected as they
imply that the slope of the concentration vs. time plot is linear up to that time. It means that the 10 mmoles of dissolved forsterite is an upper limit, and dissolution of smaller amounts may very well be expected from a real batch system under these circumstances. To put the 10 mmoles of Table 3 into perspective, it would mean dissolution of 85% of the two grams that entered the reactor in the first place, a huge percentage to enable moderate magnesite supersaturation and potential but not guaranteed precipitation. Our forsterite model clearly indicates that dissolution of forsterite under pCO2 of 100 bar and T = 100 °C will not lead to magnesite precipitation, and effectively, Giammar et al. (2005) observed no magnesite precipitation for reaction times of nearly four weeks under exactly those conditions as reported above (pCO2 100 bar, T = 95 °C, batch dissolution of forsterite in DI water, albeit at a smaller initial mass of 0.46 g). This PHREEQC exercise is not meant to duplicate real lab findings but to emphasise how hard it is to create enough alkalinity to reach carbonate supersaturation and to provide a bench mark of the magnitude of required T/p conditions to gauge in how far reported carbonisation in batch reactors may be genuine or might go back to the effect of degassing.

The conditions to reach calcite supersaturation and carbonatisation of basalts under high pCO2 in a batch system are even more demanding because of its, relative to forsterite, intrinsically lower dissolution rate at low pH combined with a lower apparent activation energy, i.e. lower T dependence of the rate constant. Akin to the forsterite model, basalt, or rather its constituents (30% glass, 20% forsterite, 30% diopside, 20% labradorite) were modelled with PHREEQC3 to dissolve under the aforementioned conditions. Again, 10 mmoles were chosen as reactant for the calculations, although Table 3 suggests a much lower amount, due to the lower dissolution rate and T of only 50 °C compared to the forsterite example. Fig. 10 summarises the findings. Analogous to Fig. 9, the dotted lines illustrate the raise in solute Ca and pH as a function of T which translates into calcite saturation indices becoming progressively less negative. However, even at 10 mmoles of reactant, the system is still quite undersaturated with respect to calcite. Not so, however, if the experiment is stopped and degassed and cooled down. Like in the case of forsterite, CO2(aq) removal will lead to calcite supersaturation. This is not too surprising given that for all modelled cases, the remaining amount of dissolved CO2 in the reactor after dissolution ceases was still >96% for the basalt and >95% for the forsterite, respectively. After all, equilibrium with a pCO2 of 100 bar creates CO2(aq) concentrations in the range of 0.8 (100 °C) to 1.1 (50 °C) moles/kg (Duan and Sun, 2003), of which roughly 1‰ dissociates to create bicarbonate and protons. As such, there is still plenty of CO2 left to degas, especially if the reactor is first degassed (still at high T where the gas solubility is considerably lower) and then later cooled. So clearly a first measure to terminate this kind of coupled dissolution and precipitation experiment needs to be the cooling of the reactor while maintaining the pressure but no mention of this procedure and its necessity is found in the relevant literature (or of any other subsequent measure to avoid the pH rise, for that matter). Degassing in this study has been presented so far as removal of CO2 and concomitant increase in pH. However, this is only half of the story why carbonatisation of basalt/forsterite in a batch reactor at such conditions as described above seems hardly avoidable.

Degassing creates a lot of tiny bubbles and these bubbles may act as catalysts for heterogeneous nucleation of the carbonates. The oil industry is very well aware of the phenomenon of ‘flash scaling’ during production of formation fluids from depth (Civan (2016) and references cited therein). Given that the fluid that permeates the sedimentary formation is expected to be at equilibrium with calcite, e.g. Hutcheon et al. (1993), any increase of its saturation during production and degassing at the bubble point will evidently promote carbonate scaling. Zhang et al. (2001) analysed a carbonate scale profile from downhole logging from a North Sea oilfield well and reported considerable carbonate scale build-up over a depth range of only 240 m, with scaling rates highest at the gas entry point of the production bore (where the gas meets the saturated fluid) and gradually declining to almost zero. It is thus plausible that such flash scaling may occur after depressurisation in a reactor too, but rarely has this subject been raised in the pertinent literature on carbonatisation of (ultra)mafic rocks/minerals in pressurised reactor experiments; a notable exception is Daval et al. (2009) who discussed the effect of ‘quenching’. Finally, another related issue that is apparently of no concern or consequence in this kind of experimental study is the headspace and its potential implications. Adding CO2 as supercritical fluid (scCO2) to the water-filled reactor below its maximum solubility (at experimental conditions) will ensure that the headspace is free of CO2 as it will all dissolve in the reactor fluid. However, many experimental studies inject CO2 either directly as a gas phase into the headspace (displacing the air in it) or use dry ice in sufficient quantities to create a gaseous headspace. Staying with the previous PHREEQC example, at 50–100 °C and pCO2 of 100 bar, this headspace, which consists basically of gaseous CO2, will turn supercritical. In how far the very diffusive scCO2 will interact with the underlying water-based fluid —and suspended fine rock/mineral particles— has only been addressed by those papers that specifically set out to investigate the effect of ‘wet’ (water-saturated) scCO2 on the matrix (usually recognisable because these studies wear the name scCO2 in the title). There are, however, a number of experimental studies on forsterite/basalt carbonatisation (always at relatively high P and T, of course), who did not address the scCO2 contribution from the headspace. This is an unfortunate omission because there is a fair number of lab studies that report that reactions between wet scCO2 and Ca/Mg-rich rocks/minerals lead to rapid carbonate mineral formation (Felmy et al., 2012; Kwak et al., 2010, 2011; Lin et al., 2007; Loring et al., 2011; Qafoku et al., 2014; Regnault et al., 2005). Perhaps some of the formed carbonates are not an artefact of the depressurisation after all but rather go back to unnoticed/undiscussed scCO2–mineral
interactions that promote CO₂ mineralisation (McGrail et al., 2009). Studying scCO₂-mineral reactions would actually be an advantage because field injections involve scCO₂ so experiments including wet scCO₂ are closer to reality. However, this needs to be acknowledged and its potential implications discussed by the experimenter. After all, scCO₂ only develops at supercritical conditions when the aqueous phase becomes supersaturated with the liquid or gaseous CO₂ that was used in the first place and that need not always be the case; many experiments simply contain dissolved CO₂(aq).

In flow-through reactors and those batch reactors that allow for fluid sampling it seems straightforward to discard degassing as a potential artefact and establish genuine carbonate precipitation during the experiment. By looking at the evolution of the solution chemistry, with a special emphasis on the non-stoichiometry of dissolution over time, it appears feasible to establish secondary phase formation. However, to stay with the case of forsterite dissolution under pCO₂ conditions, free Mg concentrations in the reactive fluid may decrease over time, but not necessarily or compellingly because it is precipitated as magnesite but alternatively because the forsterite/olivine surface becomes passivated by the precipitation of silica (Daval et al., 2009, 2011; García et al., 2010; Maher et al., 2016; Sissmann et al., 2013), slowing down the dissolution process. Likewise, the silica solute concentration may decrease over time due to silica precipitation but it may also increase because of condensation, polymerisation, and ultimately (partial) detachment of the secondary silica layer that forms on the reacted forsterite surface (De Baere et al., 2015). As such, even the non-stoichiometry of the dissolution reaction is ambiguous in its meaning and cannot be alleged as an unequivocal indication of secondary carbonate formation under experimental conditions. In the case of glassy and crystalline basalt, similar caveats apply but for other reasons. While magnesite is the principal sink for Mg in the forsterite system, the fate of solute Ca in the basaltic system is far less obvious. Decreases in the Ca solute signal cannot be ascribed to calcite formation as under hydrothermal conditions, Ca can be incorporated in other secondary phases such as zeolites or clays (Verney-Carron et al., 2015).

Equally problematic can it be to base conclusions on carbonate formation in the reactor on the solution pH. Experimenters model the saturation index of their carbonate phases during the reaction to ascertain that their system is considerably supersaturated with respect to carbonate phases. Therefore it is vital to know the pH in the pressurised and heated reactor. Although high P/T pH electrodes are commercially available that can be connected either to a batch reactor or between reactor outlet and backpressure regulator of a flow-through system to determine the in situ pH, (Galeczka et al., 2013; Wolff-Boenisch et al., 2011), this parameter is often determined indirectly from measured reactor pressure (corresponding to the pCO₂) and alkalinity. Given the large amount of lost CO₂ from the fluid the dissolved inorganic carbon (DIC) cannot be used alternatively to extrapolate pH values. But the alkalinity, too, is evidently determined after degassing the sample. There does not exist a systematic study to quantify the degree of error in the pH (and thus carbonate saturation) by this approach but studies on the reconstruction of the in situ composition of formation waters at depth may provide a clue. These studies face the same problem of trying to determine the chemistry of the formation fluid at high pressures and temperatures and the limitation of only disposing of samples that were taken after producing the fluid to the surface and degassing the sample. After reconstructing the chemical composition and in situ pH/pCO₂ of the formation waters, these studies show that reconstructed pH are invariably lower than degassed ones, in many cases more than one order of magnitude lower (Bazin et al., 1997; Palandri and Reed, 2001; Wolff-Boenisch and Evans, 2013). The difference between measured and reconstructed pH depends on the pCO₂ which in these studies never surpassed a few bars. As such, degassing of a pressurised vessel of tens or rather hundreds of bars pCO₂ will have a more deleterious effect on the pH and thus on alkalinity. Indeed, Wang and Giammar (2013) dissolved forsterite under conditions relevant to carbon sequestration and observed that the pH determined under ambient lab conditions was usually 1–2 units larger than the calculated in situ pH, due to elevated T and high pCO₂ degassing from the solution under ambient conditions. It follows that carbonate SI calculations based on indirect pH determinations derived from alkalinity measurements after degassing from this type of high pCO₂ experiment need to be viewed with scepticism.

Evidently, as earth scientists we are primarily interested in fluid-mineral interactions under in situ conditions, for example in the reservoir, or during oil, gas and geothermal production. Hence, any potential false-positive misinterpretation of pervasive carbonisation based on reactor experiments at high(er) pCO₂ and T needs to be carefully re-evaluated. This does by no means signify that all the pertinent literature is flawed—but carbonisation depends first and foremost on the degree of supersaturation to start heterogeneous nucleation and as it was shown in the preceding section it is a challenging task to create enough alkalinity solely by acidity titration using the alkaline rock/metal. Alkalinity is a double-edged sword; we need it for carbonisation but its powerful buffer capacity may freeze the pH without necessarily reaching the required threshold for sustained carbonate formation. It is the experimenter’s responsibility to establish unequivocally that the buffer capacity was overcome by natural means (dissolution) to reach considerable supersaturation but the fact that ‘degassing’ and ‘flash scaling’ are notions that are rarely discussed in this respect indicates this has not always been the case in the literature.

2. Summary

This contribution is not about rehashing the most conspicuous pitfalls that can occur during mineral dissolution/precipitation experiments, such as defect equipment, or errors introduced during flawed sampling, acidification, dilution, calibration, and analysis. It is about:

a) Not taking certain pre-requisites such as pure uncontaminated material and corrosion resistant equipment for granted, even if the provider/manufacturer touts it as such, and remain vigilant during the entire experimental course as to any unexpected solute signal that may prompt you to abort the experiment on time or look closer at potential artefacts when applying surface analytical techniques.

b) Being more critical on the genuine observations and subsequent interpretation from experiments. How likely is it that some dissolution rates are not only from one but several phases of the same sample, especially in the case of feldspars or clays; how genuine are reports of pervasive precipitations of carbonate phases from experiments under high pressure/temperature, given that most if not all observations are carried out subsequently, under ambient conditions? Were they indeed formed under the reported T/P conditions or are they artefacts of the inevitable change in conditions during termination? Because precipitation kinetics of Ca and Mg-carbonates increase substantially with the degree of supersaturation (Saldi et al., 2009; Teng et al., 2000), it is plausible and yet not properly addressed assumption that some of the reported carbonate formation in the literature may not be genuine carbonate precipitation under experimental conditions. Rather, their origin may be either


