

# Redox in Magmas: Comment on a Recent Treatment of the Kaiserstuhl Volcanics (Braunger et al., Journal of Petrology, 59, 1731–1762, 2018) and Some Other Misconceptions

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## INTRODUCTION

The recent contribution by Braunger *et al.* (2018) provides a thorough petrographic and geochemical description of peralkaline and carbonatitic igneous rocks from the Kaiserstuhl Volcanic Complex, SW Germany (KVC). These data are used to calculate several intensive variables: temperature ( $T$ ), pressure ( $P$ ), silica activity ( $a_{\text{SiO}_2}$ ), and oxygen fugacity ( $f_{\text{O}_2}$ ), which are then applied to constrain the petrogenesis of the different KVC magma series, including identifying features of their source with an emphasis on redox conditions. Using a variety of thermodynamic equilibria, Braunger *et al.* (2018) showed that the redox states of the various silicate KVC magmas in intensive-variable space follow  $T$ – $f_{\text{O}_2}$  paths that are 1 to 3 log-bar units more oxidised than the fayalite–magnetite–quartz oxygen buffer (FMQ), denoted as  $\Delta\text{FMQ} +1$  to  $+3$ . These intensive-variable redox paths are consistent with previous work on other examples of the peralkaline-carbonatitic association (e.g. Marks *et al.*, 2008, Zaitsev *et al.*, 2012). However, Braunger *et al.* (2018) then introduce a novel variation to the treatment of relative oxygen fugacities in magmas, in which they present their results ‘relative to  $a_{\text{SiO}_2}$ -corrected buffer curves, expressed as  $\Delta\text{FMQ}^*$ . The seemingly high values of this latter variable are caused by low  $a_{\text{SiO}_2}$  rather than unusually high  $f_{\text{O}_2}$ , which invalidates their inference that ‘oxidizing and carbonated fluids/melts interacting with the mantle lithosphere is a major prerequisite for the subsequent genesis of mixed alkaline silicate rock-carbonatite complexes’. The carbonatites themselves are identified by Braunger *et al.* (2018) as even more oxidised, because

they have  $\Delta\text{FMQ}^* \approx 6$ , even though they equilibrated at an entirely unexceptional  $f_{\text{O}_2}$  for igneous rocks ( $\Delta\text{FMQ} = \pm 2$ ). Braunger *et al.* (2018) interpret the strongly positive  $\Delta\text{FMQ}^*$  as evidence for a particularly oxidized mantle source. Here we argue that the concept of  $\Delta\text{FMQ}^*$  does not support any of these inferences; indeed it is unlikely ever to support anything, being physically meaningless. We also take the opportunity to reiterate that to relate a chemical potential in a magma such as  $f_{\text{O}_2}$  to its value in the source is not a simple exercise, but requires a great deal of petrological modelling of the relevant compositional variables. Even where such modelling is feasible, it rests on assumptions that present petrologic knowledge may be insufficient to validate.

## OXYGEN FUGACITY IN MAGMAS

The redox state of a natural magmatic liquid is intimately related to its ratio of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ , as given by the reaction:



The importance of this ratio in terrestrial magmas is due to the abundance of Fe being far greater than other redox-variable elements. Oxygen fugacity may be calculated from the equilibrium constant of this reaction:

$$0.25 \log f_{\text{O}_2} = -\log K + \frac{a_{\text{Fe}^{3+}\text{O}_{1.5}}}{a_{\text{Fe}^{2+}\text{O}}} \quad (2)$$

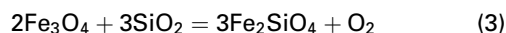
This reaction has been calibrated experimentally in many studies over many decades, and is still attracting

experimental attention because of its importance in igneous petrology (e.g. [Borisov et al., 2018](#)). These calibrations may be applied to igneous rocks to calculate  $fO_2$  from measured  $Fe^{3+}/Fe^{2+}$  ratios, most readily for natural glasses because of the relative ease with which  $Fe^{3+}/Fe^{2+}$  can be measured, although the fine details are not entirely uncontroversial (e.g. [Berry et al., 2018](#)). But determining reliable  $Fe^{3+}/Fe^{2+}$  in crystalline igneous rocks is subject to many more difficulties, both analytical and to do with the uncertainties attendant on whether the bulk composition represents the liquid composition (i.e. phenocrysts, xenocrysts, antecrysts, volatile loss, etc.). Therefore,  $fO_2$  is often estimated from the compositions of liquidus phases, notably coexisting Fe–Ti-oxides where available ([Buddington & Lindsley, 1964](#); [Ghiorsio & Evans, 2008](#)), but making use of other equilibria as the situation allows, as for example has been successfully done by [Braunger et al. \(2018\)](#). In these cases it may be difficult to translate the calculated  $fO_2$  into  $Fe^{3+}/Fe^{2+}$  ratios, and often this is not attempted. This has led to an emphasis on reporting the  $fO_2$  of magmas, but for many petrological applications it is the  $Fe^{3+}/Fe^{2+}$  of the magmatic system that is the required information. Knowledge of  $fO_2$  is insufficient for understanding the origin and evolution of the redox states of the magmas, although it can be used for bypassing  $Fe^{3+}/Fe^{2+}$  in the evaluation of the redox speciation of other polyvalent elements (H, C, S, Cr, V, Eu), or the composition of gases evolving from the magma, if amounts are sufficiently small not to change  $Fe^{3+}/Fe^{2+}$ . Unfortunately, the relationship between  $Fe^{3+}/Fe^{2+}$  and  $fO_2$  is sometimes turned around, to attribute, erroneously, properties of the magmas to  $fO_2$  when it is redox speciation that is the controlling variable. It has been long recognised that the  $fO_2$  of a natural rock is simply a reflection of whatever ratios of redox-sensitive elements the rock contains, under the simplifying assumption that the rock is a system at equilibrium (e.g. [Ohmoto & Kerrick, 1977](#)). [Braunger et al. \(2018\)](#) do not give the redox speciation of Fe in the KVC magmas but report only  $fO_2$ , in the form  $\Delta FMQ$ .

## OXYGEN BUFFERS

[Braunger et al. \(2018\)](#) state that ‘... the use of  $\Delta FMQ$  is not consistent in the literature’. They do not explain what the inconsistencies are, or provide examples, and we disagree—the term has for many decades been applied without ambiguity to denote a chemical equilibrium that serves as a reference state. As far as we can ascertain, departure from this accepted usage is unique to [Braunger et al. \(2018\)](#), as revealed by their statement that ‘Importantly, this buffer curve is also strongly  $aSiO_2$ -dependent and may shift by several log units’. This is a contradiction in terms. For a buffer to shift by several log units would mean that it is not a buffer.

The FMQ equilibrium is defined by the following reaction ([Darken, 1948](#)):



An equilibrium constant  $K_{FMQ}$  can be formulated as:

$$K_{FMQ} = \frac{a_{Fe_2SiO_4}^3 \times fO_2}{a_{Fe_3O_4}^2 \times a_{SiO_2}^3} \quad (4)$$

This equilibrium is petrologically useful in multiple ways. Firstly, when fayalite, magnetite and quartz are present as pure phases in experiments, control of  $fO_2$  is achieved. Secondly, when the activities of these components are determined by measurements on natural olivine and spinel with known  $aSiO_2$  (e.g. from the olivine–orthopyroxene equilibrium), it is possible to determine  $fO_2$  in rocks. Thirdly, as most natural igneous rocks equilibrate at  $fO_2$  conditions close to the FMQ buffer, it is a useful reference point. Whilst all three applications are related through [equation \(4\)](#), they are not the same. [Braunger et al. \(2018\)](#) have confused the equilibrium describing a low-variance phase assemblage on which an oxygen buffer is based (i.e. FMQ) with the equilibrium between its components in multi-component compositional space with many degrees of freedom. To explain this further, some historical perspective is necessary.

The problems begin with what is meant by an ‘oxygen buffer’. There appears to be a lack of any concise but authoritative definition in the petrological literature, likely due to the history of this concept. However, [Frost \(1991\)](#) gave a most useful review, in which a definition is implicit. According to [Frost \(1991\)](#) the use of the term ‘oxygen buffer’ in petrology originated in experimental petrology: ‘the concept of oxygen fugacity was introduced to petrology by Hans Eugster ... in experimental runs ([Eugster, 1957](#))’. [Frost \(1991\)](#) pointed out later in his review, this is not completely correct because Eugster referred to the partial pressure of  $O_2$  ( $pO_2$ ), which was a mistake on Eugster’s part. He clearly meant oxygen fugacity ( $fO_2$ ). Here we note that  $fO_2$  is equivalent to the chemical potential of oxygen ( $\mu_{O_2}$ ), through the definition:

$$\mu_{O_2} \equiv \mu_{O_2}^\circ + RT \ln \frac{fO_2}{pO_2^\circ} \quad (5)$$

where  $pO_2^\circ$  is the pressure of the ideal gas at the standard state pressure of one bar and the temperature of interest. It is important to emphasise that this definition does not imply the presence of a gas or fluid phase in the system of interest, even though a gas is used as a reference state. Fugacity should not be viewed as some kind of pressure, although it has the units of pressure.

[Equation \(5\)](#) is an identity, and in what follows we treat oxygen fugacity as a chemical potential expressed in another form and quantified in different units. But partial pressures are a different concept. They are equivalent to fugacities only for an ideal gas, and it is this factor that permits the standard state in [equation \(5\)](#) to be designated as a partial pressure,  $pO_2^\circ$ . The confusion may have arisen because the C–O and C–O–H

gas mixtures used to control  $f\text{O}_2$  in experiments at high temperatures and near-ambient pressures are very close to ideal gases (e.g. Darken & Gurry, 1945; Muan, 1955), making  $f\text{O}_2$  and  $p\text{O}_2$  interchangeable. But at higher pressures, the numerical value of  $f\text{O}_2$  may be nowhere near  $p\text{O}_2$ . For example, considering pure  $\text{O}_2$  gas, Berry *et al.* (2003), using the data of Belonoshko & Saxena (1991), calculated a value of  $f\text{O}_2 = 10^{4.8}$  bar ( $= 63.1$  GPa) at  $p\text{O}_2 = 10^{3.04}$  bar ( $= 1.1$  GPa). In the follow-up to his short 1957 paper, Eugster (1959) elaborated his discussion of ' $p\text{O}_2$ ' in experimental systems including hydrothermal systems, and in a further petrological landmark applied the concept to natural rocks. Curiously,  $\mu\text{O}_2$  is mentioned in this paper but its relationship with  $p\text{O}_2$  or  $f\text{O}_2$  is not alluded to. The concepts of  $f\text{O}_2$  and/or  $\mu\text{O}_2$  became accepted as an important variable in experimental petrology soon after (Ernst, 1960; Eugster & Wones, 1962). These latter papers clarified that the desired variable in high-pressure contexts should be  $f\text{O}_2$ , not  $p\text{O}_2$ . The early recognition that  $f\text{O}_2 \neq p\text{O}_2$  is occasionally forgotten, leading to erroneous statements on the equivalence of  $f\text{O}_2$  and  $p\text{O}_2$  in the literature (e.g. the recent report by Li *et al.*, 2019).

Eugster and co-workers needed to control  $\text{Fe}^{3+}/\text{Fe}^{2+}$  in their experiments, a challenge faced by many early experimental petrologists in ambient-pressure experiments (Bowen & Schairer, 1932; Roedder, 1951; Allen & Snow, 1955). This required the control of  $f\text{O}_2$ , which may be done by equilibrating the system of interest with a reservoir in which  $f\text{O}_2$  is kept constant. A constant  $f\text{O}_2$  reservoir may be achieved in two ways, not mutually exclusive. One possibility is to design the reservoir to be so much more massive than the system of interest that the reservoir's composition changes negligibly with transfer of oxygen (or other redox sensitive species) between the reservoir and the system. An example from experimental petrology is a C–O–H gas mixture flowing over a sample in a one-atmosphere muffle furnace. The second possibility is for the reservoir to be a low-variance phase assemblage, in which the chemical potentials, including  $f\text{O}_2$ , do not change, even though the reservoir's composition changes due to equilibration with the system of interest. In introducing this latter approach, Eugster called his low-variance phase assemblages 'oxygen buffers'. He did not give a reason for his terminology, but 'buffer' is commonly used in chemistry, for example, to control pH in aqueous solutions, and this is the obvious etymology.

From the perspective of the phase rule ( $F = \Phi - C + 2$ ), the requirement is two degrees of freedom (that is,  $F = 2$ , divariant, meaning that the buffer works for any combination of  $P$  and  $T$ ). One of the components ( $C$ ) is oxygen, hence oxygen buffers are commonly systems of two condensed phases ( $\Phi$ ), comprised of oxygen and one other component, or three condensed phases and two other components. If any gas or fluid phase is present, it is omitted from this accounting. The examples of oxygen buffers

given by Eugster (1957) were two-phase assemblages in the two-component system Fe–O (iron–wüstite, wüstite–magnetite, magnetite–hematite), and the three-phase FMQ assemblage in the three-component system Fe–SiO<sub>2</sub>–O. In practice, the  $F = 2$  stipulation mostly excludes phases of variable composition, although wüstite,  $\text{Fe}_{1-x}\text{O}$ , is an obvious exception, as would be any phase where the non-stoichiometry was due to oxygen content.

### Oxygen buffers as reference curves in $T$ – $f\text{O}_2$ space

Aside from experimental petrology, the divariant assemblages that form oxygen buffers have found another use in petrology, by providing reference states for petrologically deduced values of  $f\text{O}_2$  in rocks. This is a matter of convenience, not necessity, which arises for the following reason. Like all chemical potentials,  $\mu\text{O}_2$  (hence  $f\text{O}_2$ ) is only quantifiable relative to a standard state, which is by convention  $p\text{O}_2^\circ$  (equation 3). The chemical environment of oxygen in this standard state, a diatomic molecule in a tenuous gas, is nothing like that of oxygen in the minerals and melts of magmatic systems, where it occurs as an anion ( $\text{O}^{2-}$ ) bonded to cations. Not surprisingly, temperature changes manifest themselves on the behaviour of  $\text{O}_2$  molecules in a tenuous gas very differently to the behaviour of  $\text{O}^{2-}$  anions in condensed phases. One of many consequences is that the heat capacity ( $C_V$ ) of an ideal diatomic gas such as low-pressure  $\text{O}_2$  is  $5/2 R$ , or  $5/4 R$  per mole of O, whereas the Dulong–Petit value of  $3 R$  per mole of O is a good approximation for the entire mineral kingdom at high temperature. The consequence of interest here is the way the ratio  $f\text{O}_2/p\text{O}_2^\circ$  changes with temperature, when the  $f\text{O}_2$  is defined by a system of condensed phases. This ratio changes a lot, with the result that reporting a value of  $f\text{O}_2$  for a mineral assemblage without specifying temperature is worse than meaningless—it is actively confusing (e.g. Lindsley, 1976). For example, if a siliceous ironstone equilibrated with a reservoir with an  $f\text{O}_2$  of  $10^{-15}$  bars at  $1100^\circ\text{C}$ , its redox state would be too reducing for  $\text{Fe}_2\text{SiO}_4$  (fayalite) to be stable, with this phase breaking down to Fe metal plus silica (quartz). Conversely, if the ironstone equilibrated with a reservoir at the same value of  $f\text{O}_2$  of  $10^{-15}$  bars, but at  $700^\circ\text{C}$ , not  $1100^\circ\text{C}$ , its redox state would be too oxidising for  $\text{Fe}_2\text{SiO}_4$  to be stable, breaking down to  $\text{Fe}_3\text{O}_4$  plus quartz. Even then, a numerical  $T$ – $f\text{O}_2$  combination is challenging to interpret unless a relevant diagram is available nearby or one has managed to memorise  $T$ – $f\text{O}_2$  space (Haggerty, 1976). In order to minimise the opportunities for confusion, it has become customary to switch standard states from  $\text{O}_2$  ideal gas to an experimentally calibrated divariant ( $F = 2$ ) oxygen buffer. This works as follows: using the definition of  $f\text{O}_2$  in equation (5), we can define  $f\text{O}_2$  both for the rock and for a selected but arbitrary divariant oxygen buffer,

subtract the latter from the former, and with rearrangement obtain:

$$\log \frac{f\text{O}_2^{\text{rock}}}{f\text{O}_2^{\text{buffer}}} \equiv \frac{\mu\text{O}_2^{\text{rock}} - \mu\text{O}_2^{\text{buffer}}}{2 \cdot 303RT} \quad (6)$$

Note that the terms referring to ideal  $\text{O}_2$  gas in [equation \(5\)](#), namely  $\mu\text{O}_2^\circ$  and  $p\text{O}_2^\circ$ , do not appear, having cancelled out. The identity of the divariant oxygen buffer is unimportant, and can be chosen without assuming any connection to the rock, just like ideal  $\text{O}_2$  gas at 1 bar has no connection to the rock. The fundamental misconception that fugacity is physically some sort of partial pressure has occasionally led petrologists to calculate (erroneously) the number of molecules of  $\text{O}_2$  in a volume of rock at a given  $f\text{O}_2$  (e.g. [Giggenbach, 1992](#)), but even to attempt this is to misunderstand that fugacity is a chemical potential—not a pressure—and, moreover, no gas (or fluid) phase is necessary for its definition. The value of  $f\text{O}_2^{\text{buffer}}$  in [equation \(6\)](#) should be viewed as just a convenient thermodynamic reference state. For example, the divariant assemblage chosen by [Christie et al. \(1986\)](#) in their classic paper on the redox states of mid-ocean ridge basaltic (MORB) glasses was the Ni–NiO oxygen buffer (see [Christie et al., 1986](#), their Figs. 5 and 6). The quantity  $\log(f\text{O}_2^{\text{rock}}/f\text{O}_2^{\text{Ni-NiO}})$  is abbreviated as  $\Delta\text{NNO}$ . There is no implication that MORB glasses have a particular activity (chemical potential) of Ni or NiO, as indeed they do not.

For the aforementioned siliceous ironstone at  $1100^\circ\text{C}$ ,  $f\text{O}_2 = 10^{-15}$  bars, the value of  $\Delta\text{NNO}$  is  $-6.1$ , whereas at  $700^\circ\text{C}$ ,  $f\text{O}_2 = 10^{-15}$  bars,  $\Delta\text{NNO}$  is  $+1.3$ . So just by changing the reference state, the distinction between an oxidising redox environment and a reducing redox environment is made apparent without having to specify temperature precisely. Most petrologists have a good mental conception of the mineral assemblages and compositions to expect around a buffer. For example, an arc magma equilibrated at  $f\text{O}_2$  values equivalent to  $\Delta\text{NNO} = +2$  can be intuitively understood as highly oxidised (e.g. containing sulfate and magnetite), whereas a mantle xenolith equilibrated at  $f\text{O}_2$  values equivalent to  $\Delta\text{NNO} = -4$  can be intuitively understood to be rather reduced (e.g. containing sulfide and  $\text{Fe}^{3+}$ -poor spinels). This is obviously useful in discussing redox relations in magma series evolving over a range of temperature, including those of the KVC province studied by [Braunger et al. \(2018\)](#).

The thermochemical reason why oxygen buffers mostly have similar slopes in  $T$ – $f\text{O}_2$  space can be understood from the van 't Hoff relation:

$$\frac{d \log f\text{O}_2}{dT} = -\frac{\Delta H^\circ}{2 \cdot 303RT^2} \quad (7)$$

Integrating this equation under the customary approximation that  $\Delta H$  is constant between two temperatures  $T_1$  and  $T_2$ , firstly for  $f\text{O}_2$  in a rock and then for Ni–NiO, and subtracting the latter from the former, gives:

$$\Delta\text{NNO}_{T_1} - \Delta\text{NNO}_{T_2} = -(\Delta H_{\text{rock}} - \Delta H_{\text{NNO}}) \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (8)$$

Therefore, the smaller the difference between the enthalpy of the reaction determining  $f\text{O}_2$  in the rock [e.g. [equation \(1\)](#) in a silicate magma] and the enthalpy of the oxygen buffer equilibrium, here of Ni–NiO, the more nearly constant will be  $\Delta\text{NNO}$  as a function of temperature. It also helps if the temperature regime under consideration, namely  $(T_1 + T_2)/2$ , is high, as for magmas.

Although the Ni–NiO buffer has been used fairly often as the reference state for  $f\text{O}_2$  in petrology, the FMQ oxygen buffer is even more popular. We are aware of three reasons, the most important of which is that the enthalpy of reaction of this buffer appears identical within experimental uncertainty to that of [equation \(1\)](#) for basaltic liquids ([O'Neill et al., 2018](#)), such that although the change of  $\Delta\text{NNO}$  with  $T$  for a silicate melt of constant  $\text{Fe}^{3+}/\text{Fe}^{2+}$  is small, the change of  $\Delta\text{FMQ}$  is sensibly zero. Secondly, it has long been noted that most terrestrial igneous rocks record equilibration in  $T$ – $f\text{O}_2$  space close to the FMQ buffer ([Haggerty, 1976](#)). Thirdly, the FMQ divariant assemblage is the thermodynamic equilibrium from which values of  $f\text{O}_2$  for the common upper mantle phase assemblage of olivine, orthopyroxene and spinel are calculated ([O'Neill & Wall, 1987](#)).

None of these considerations is particularly compelling. The downside to using FMQ rather than NNO is that the thermodynamic data for the former have higher uncertainty, which is in part a reflection of discrepancies among experimental calibrations of the FMQ equilibrium ([O'Neill, 1987](#)). Also, the fayalite–magnetite–quartz assemblage melts at rather low temperature [ $1118^\circ\text{C}$  at atmospheric pressure, according to [Darken \(1948\)](#)], requiring extrapolation of the thermodynamic data if the FMQ reference is to be used at higher temperatures. Although these are minor issues in comparison with the uncertainties attendant on calculating  $f\text{O}_2$ s in rocks, it would be good practice for all who report  $f\text{O}_2$  values relative to any buffer (FMQ or others) to state the reference values, similar to the common practice of reporting the source of normalisation factors in normalised trace element variation diagrams.

### Oxygen sensors versus oxygen buffers

In his section on 'Common Misconceptions', [Frost \(1991\)](#) warned that 'Oxygen buffers rarely exist in nature. Thus, when one says "Rock A equilibrated to oxygen fugacities on the NiNiO buffer" one really means that Rock A equilibrated at oxygen fugacities equivalent to those of the NiNiO buffer. This seems to be a trivial point, but it is important to understand the difference between the behaviour of oxygen fugacity in an experimental charge and its behaviour in geological systems'. Frost's point could equally have been made using FMQ rather than NNO, which might have made it seem less trivial. Natural systems encompass equilibria that may



be used to calculate their  $fO_2$ ; for example, Braunger *et al.* (2018) list eight such equilibria as potentially suitable for calculating  $fO_2$  in their rocks. Given that such equilibria are selected because they involve  $fO_2$ , each would also be an oxygen buffer in a simple system, limited only to those components partaking in the equilibrium, but are not buffers when applied to systems with more degrees of freedom, containing phases that may be of variable composition. And in igneous rocks there are always many more degrees of freedom. Context is everything. A buffer imposes or controls  $fO_2$ , whereas a sensor measures it. This distinction is why the statement 'this buffer curve is also strongly  $aSiO_2$ -dependent' is a contradiction in terms. It is the number of degrees of freedom of the system that determines whether an equilibrium is acting as a buffer rather than a sensor. The distinction is easy to spot in experimental petrology, where using equilibria with more degrees of freedom than two ( $F > 2$ ) to sense  $fO_2$ , as opposed to controlling it, requires the experimenter to adopt a different experimental configuration. Several well-known experimental  $fO_2$  sensors have just three degrees of freedom. Examples are NiO–NiPd, in which  $fO_2$  is measured by the displacement of the Ni–NiO equilibrium in  $T$ – $fO_2$  space by alloying of Pd with Ni (e.g. Scaillet & Evans, 1999), and Fe–Ti-oxides, in which both condensed phases (spinel and rhombohedral oxide) are solid solutions (e.g. Carmichael, 1966; Anenburg & Mavrogenes, 2016).

For the sake of completeness, we should mention that there could be instances where the distinction between buffer and sensor might become blurred. Buffering of oxygen requires that  $\mu O_2$  is constant, i.e.  $\partial\mu O_2/\partial n O_2$  is zero over a reasonable interval  $\Delta n O_2$ . However, if  $\partial\mu O_2/\partial n O_2$  is small, the system could be viewed as being approximately buffered. Use of the word 'buffer' in such a context is a value judgement. What is mistaken is to assume that because  $\Delta FMQ$  (or  $\Delta NNO$ , etc.) is constant for a rock suite, the suite is buffered. This fallacy, which has had a most deleterious influence in igneous petrology, possibly derives from the seminal work on the global distribution of redox states in MORB glasses by Christie *et al.* (1986), which showed that their  $Fe^{3+}/\Sigma Fe$  (hence  $\Delta NNO$ ) hardly changed with indicators of igneous differentiation (like MgO concentration). This observation, which has stood the test of time (e.g. O'Neill *et al.*, 2018), gave rise to the idea that these basaltic magmas were buffered in  $fO_2$ , perhaps by interaction with country rock (i.e. the country rock is a reservoir, Carmichael & Ghiorso, 1986). With further work it has become apparent that the nearly constant  $\Delta FMQ$  is due to the similarity in bulk mineral/melt partition coefficients of  $Fe^{2+}$  and  $Fe^{3+}$  in MORB magmas crystallising their standard cotectic assemblage of olivine, plagioclase and clinopyroxene (O'Neill *et al.*, 2018). In other words,  $Fe^{3+}$  just happened to be incompatible precisely to the degree that preserves  $\Delta FMQ$ , and the magmas are not buffered. To quote Frost (1991) again: 'When one finds that a suite of rocks defines a  $T$ – $fO_2$

trend that lies on that of the NNO buffer, it is important to note that it is entirely a coincidence that has nothing to do with the NNO buffer'.

## INFERRING THE REDOX STATE OF MAGMA SOURCES

Partial melting and the production of magma thereby is essentially an irreversible process, not least because it occurs in a gravitational field (Ganguly, 2005). Melts from the mantle are usually modelled as the products of accumulated near-fractional melting (McKenzie & Bickle, 1988), itself an irreversible process. Lastly, the  $fO_2$ – $P$  path followed by a basaltic magma from source to surface is steeper than that of solid mineral assemblages, and unlike  $fO_2$ – $T$  paths,  $fO_2$ – $P$  paths of magmas differ from oxygen buffers like FMQ (e.g. O'Neill *et al.*, 2006). The net result is that the  $\Delta FMQ$  of a magma is not that of its source, except by coincidence. In fact, even to talk about a source rock having a specific  $fO_2$  is misleading, because this intensive variable changes with  $P$ ,  $T$  and degree of melting under closed system conditions (constant bulk composition), due to the changing distribution of redox-sensitive species (mainly  $Fe^{2+}$  and  $Fe^{3+}$ ) among the phases of the system, and other changes in the compositions of these phases themselves. Obviously, in upper-mantle spinel lherzolite, where  $fO_2$  is given by the phase assemblage olivine–orthopyroxene–spinel through the FMQ equilibrium, the activity of the  $Fe_3O_4$  component in spinel is critical. But spinel is only a minor phase (~2% modal abundance), making its composition particularly sensitive to the solubility of Al and Cr in coexisting pyroxenes, which change with  $P$  and  $T$ . For illustration of the kind of degree of complexity in relating  $fO_2$  to  $Fe^{3+}/Fe^{2+}$  that is plausible during mantle melting, see Gaetani (2016). Gaetani's calculations address only the simple case in which the system is closed to oxygen; the open-system behaviour inherent in 'redox melting' (Foley, 2011), is necessarily even more complicated.

The variable required for modelling redox relations during partial melting of the Earth's mantle is oxygen content (more-or-less equivalent to  $Fe^{3+}/Fe^{2+}$  in most situations), not  $fO_2$ . On the other hand,  $fO_2$  is needed for evaluating transport properties of minerals and speciation of redox-sensitive minor and trace elements. So, for understanding the mantle, both frames of reference are needed. It is, however, not easy to calculate one from the other. Given the bulk composition of a rock, including its oxygen content (assumed effectively to be given by  $Fe^{3+}/Fe^{2+}$  for a simple-system approximation to the rock),  $fO_2$  will depend on the amounts and compositions of the minerals that this bulk composition will crystallise at given  $P$  and  $T$ , assuming equilibrium; this is the classic Gibbs free energy minimisation problem (Connolly, 2017). The data include activity–composition relations. The reverse problem, calculation of  $Fe^{3+}/Fe^{2+}$  for a given  $fO_2$ , may be computationally less arduous, but still depends on some of the same thermodynamic

data, namely the data for the phase components appearing in equilibria selected to define  $fO_2$  (for example, the components listed in reactions 8 to 15 of Braunger *et al.*, 2018). In both cases, the results are only as good as the necessary thermodynamic data allow. Due to analytical and related difficulties, thermodynamic data for  $Fe^{3+}$ -containing components in complex solid solutions like pyroxenes and amphiboles are relatively poorly known. The  $Fe^{3+}/Fe^{2+}$  in magmas does not depend solely on  $fO_2$ ,  $P$  and  $T$ , but also on the magma composition. For example, peralkaline melts are known to stabilise higher oxidation states of redox-sensitive elements (Giuli *et al.*, 2012; Anenburg & Le Losq, 2019), increasing the difficulty of  $fO_2$  interpretation in the alkaline KVC magmatic system.

Braunger *et al.* (2018) claim that their results 'imply highly oxidized parental source regions for carbonatites'. Putting aside that this statement rests on their unexamined and unsupported interpretation of the composite variable  $\Delta FMQ^*$ , they do not attempt the considerable modelling effort needed to infer the oxidation state of the 'source' of KVC carbonatites from their  $fO_2$  on eruption. It is also unclear if they mean the source prior to melt extraction, or, more relevant to the redox state of the carbonatites, the residue after melt extraction. The two may be expected to be different.

### MISUSE OF FMQ BY BRAUNGER ET AL. (2018)

The rationale for introducing the variable  $\Delta FMQ^*$  by Braunger *et al.* (2018) appears to stem from the equilibrium reaction underpinning the FMQ buffer.  $K_{FMQ}$  is constant at fixed  $P$  and  $T$ , and a change in any one of the variables in equation (4) requires a change in another to maintain the constant value of  $K_{FMQ}$ . As Braunger *et al.* (2018) were able to measure  $aSiO_2$  for their rocks, they recalculated the FMQ curve for equation (3) to derive a 'corrected' FMQ buffer for each rock, plotting the new curves in  $T$ - $fO_2$  space. Finally, they reported their measured  $fO_2$  values relative to these modified 'buffer'-curves (which they term as  $\Delta FMQ^*$ ) instead of the standard FMQ (in which the activities of all condensed components equal unity). As  $aSiO_2$  appears in the denominator and  $fO_2$  appears in the numerator, any decrease in  $aSiO_2$  triggers a decrease in  $fO_2$  in order to keep  $K_{FMQ}$  constant. Therefore,  $\Delta FMQ^*$ , as calculated by Braunger *et al.* (2018), is always lower than  $\Delta FMQ$ , resulting in more positive values for  $fO_2$  referenced to  $\Delta FMQ^*$ . The rocks studied by Braunger *et al.* (2018) are silica-undersaturated (e.g. nephelinites, carbonatites, phonolites, etc.), which leads to  $\Delta FMQ^*$  much greater than  $\Delta FMQ$ . The most extreme case is that of the carbonatites, which equilibrated at  $\Delta FMQ \approx 0$ , but  $\Delta FMQ^* \approx 6$ .

The 'correction' has no significance beyond its definition as  $\Delta FMQ^* = \Delta FMQ + 3\log(aSiO_2)$ . The confusion would likely not have arisen if they had reported the results of their  $fO_2$  calculations as  $\Delta NNO$  rather than

$\Delta FMQ$ . Their calculations of  $fO_2$  already take  $aSiO_2$  into account. Braunger *et al.* (2018) measured the compositions of their spinel and olivine and correctly take the  $Fe_2SiO_4$  or  $Fe_3O_4$  activities into account when calculating  $fO_2$ . But, they do not explain why they selected  $aSiO_2$  alone, and not  $aFe_2SiO_4$  or  $aFe_3O_4$ , to calculate their  $\Delta FMQ^*$ . For example, inclusion of  $aFe_2SiO_4$  in the 'correction' would result in the KVC rocks appearing reduced rather than oxidised, as claimed by Braunger *et al.* (2018). As mentioned above, reporting  $fO_2$  relative to a divariant oxygen buffer is a matter of convenience because it provides an easy-to-interpret common language for petrologists. Braunger *et al.* (2018) used FMQ because, although an arbitrary choice, it is widely known in the petrological community as a standard reference point. Applying a 'correction' defeats the purpose of FMQ being such a standard reference point. It is incorrect that the KVC rocks are highly oxidized. When compared to other igneous suites on the standard  $\Delta FMQ$  scale (e.g. Haggerty, 1976), most of the KVC rocks are only slightly oxidised with  $\Delta FMQ = +1$  to  $+2$ , well within the range expected for mantle rocks (Frost & McCammon, 2008). The carbonatites and melilitites are even somewhat reduced with  $\Delta FMQ$  values as low as  $-2$ . They write '... oxidized mantle regions... can reach  $fO_2$  of up to  $\Delta FMQ = +3.5$  (Foley, 2011...) even without considering the silica-corrected FMQ-buffer' (Braunger *et al.*, 2018), implying that the KVC rocks are exceptionally oxidised. However, their calculated  $fO_2$  values on the non-corrected  $\Delta FMQ$  scale (which is, in fact, the correct scale) are 1 to 2 log values below the maximum values described by Foley (2011) for their presumed mantle source. As stated earlier, it is not possible to assume that  $fO_2$  measured for crustal igneous rocks equals that of their mantle source region, without appropriate modelling work. As thermodynamic data for  $Fe^{3+}$  partitioning in carbonatitic systems do not exist, such modelling is not even possible at this time. The Braunger *et al.* (2018) data do not support a particularly oxidised lithospheric mantle for carbonatite generation, as claimed in their work. Moreover, the large range of  $fO_2$  values encountered in the KVC carbonatites (five orders of magnitude) compared to more tightly constrained  $fO_2$  values for the silicate rocks in their study, calls into question whether the minerals used to estimate  $fO_2$  are in equilibrium. Carbonatites are increasingly understood to represent non-equilibrium cumulate assemblages (Xu *et al.*, 2007; Chakhmouradian *et al.*, 2016; Chakhmouradian *et al.*, 2017; Anenburg & Mavrogenes, 2018; Chebotarev *et al.*, 2019). The degree to which meaningful thermodynamic variables can be extracted from compositions of carbonatite-hosted minerals is, therefore, limited.

### CONCLUSIONS

In light of our discussion, we offer a working definition of an oxygen buffer: an oxygen buffer is a divariant phase assemblage, often but not necessarily external to

the system of interest, that fixes  $fO_2$  at a constant value at a given temperature and pressure. A metamorphosed ironstone containing magnetite and hematite provides an instance of a rock with an internal buffer (neglecting minor components), but it has been beyond our capabilities to find any example of a natural system with an external buffer of the type introduced to experimental petrology by Eugster (1957). Given the chemical complexity of magmatic systems (e.g. in comparison with ironstones), we are doubtful that the buffering of  $fO_2$  would ever happen in natural settings.

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## REFERENCES

- Allen, W. C. & Snow, R. B. (1955). The orthosilicate-iron oxide portion of the system  $CaO$ – $FeO$ – $SiO_2$ . *Journal of the American Ceramic Society* **38**, 264–280.
- Anenburg, M. & Le Losq, C. (2019). Perrhenate sodalite growth from alkali silicate melts by noble metal catalysis. *SN Applied Sciences* **1**, 372.
- Anenburg, M. & Mavrogenes, J. A. (2016). Experimental observations on noble metal nanonuggets and Fe–Ti oxides, and the transport of platinum group elements in silicate melts. *Geochimica et Cosmochimica Acta* **192**, 258–278.
- Anenburg, M. & Mavrogenes, J. A. (2018). Carbonatitic versus hydrothermal origin for fluorapatite REE–Th deposits: Experimental study of REE transport and crustal “antiskarn” metasomatism. *American Journal of Science* **318**, 335–366.
- Belonoshko, A. & Saxena, S. K. (1991). A molecular dynamics study of the pressure–volume–temperature properties of supercritical fluids: II.  $CO_2$ ,  $CH_4$ ,  $CO$ ,  $O_2$ , and  $H_2$ . *Geochimica et Cosmochimica Acta* **55**, 3191–3208.
- Berry, A. J., O'Neill, H. S. C., Jayasuriya, K. D., Campbell, S. J. & Foran, G. J. (2003). XANES calibrations for the oxidation state of iron in a silicate glass. *American Mineralogist* **88**, 967–977.
- Berry, A. J., Stewart, G. A., O'Neill, H. S. C., Mallmann, G. & Mosselmans, J. F. W. (2018). A re-assessment of the oxidation state of iron in MORB glasses. *Earth and Planetary Science Letters* **483**, 114–123.
- Borisov, A., Behrens, H. & Holtz, F. (2018). Ferric/ferrous ratio in silicate melts: a new model for 1 atm data with special emphasis on the effects of melt composition. *Contributions to Mineralogy and Petrology* **173**, 98.
- Bowen, N. L. & Schairer, J. F. (1932). The system,  $FeO$ – $SiO_2$ . *American Journal of Science* **55**, 24, 177–213.
- Braunger, S., Marks, M. A. W., Walter, B. F., Neubauer, R., Reich, R., Wenzel, T., Parsapoor, A. & Markl, G. (2018). The petrology of the Kaiserstuhl Volcanic Complex, SW Germany: The importance of metasomatized and oxidized lithospheric mantle for carbonatite generation. *Journal of Petrology* **59**, 1731–1762.
- Buddington, A. F. & Lindsley, D. H. (1964). Iron-titanium oxide minerals and synthetic equivalents. *Journal of Petrology* **5**, 310–357.
- Carmichael, I. S. E. (1966). The iron-titanium oxides of salic volcanic rocks and their associated ferromagnesian silicates. *Contributions to Mineralogy and Petrology* **14**, 36–64.
- Carmichael, I. S. E. & Ghiorso, M. S. (1986). Oxidation–reduction relations in basic magma: a case for homogeneous equilibria. *Earth and Planetary Science Letters* **78**, 200–210.
- Chakhmouradian, A. R., Reguir, E. P. & Zaitsev, A. N. (2016). Calcite and dolomite in intrusive carbonatites. I. Textural variations. *Mineralogy and Petrology* **110**, 333–360.
- Chakhmouradian, A. R., Reguir, E. P., Zaitsev, A. N., Couëslan, C., Xu, C., Kynický, J., Mumin, A. H. & Yang, P. (2017). Apatite in carbonatitic rocks: Compositional variation, zoning, element partitioning and petrogenetic significance. *Lithos* **274–275**, 188–213.
- Chebotaev, D. A., Veksler, I. V., Wohlgemuth-Ueberwasser, C., Doroshkevich, A. G. & Koch-Müller, M. (2019). Experimental study of trace element distribution between calcite, fluorite and carbonatitic melt in the system  $CaCO_3 + CaF_2 + Na_2CO_3 \pm Ca_3(PO_4)_2$  at 100 MPa. *Contributions to Mineralogy and Petrology* **174**, 4.
- Christie, D. M., Carmichael, I. S. E. & Langmuir, C. H. (1986). Oxidation states of mid-ocean ridge basalt glasses. *Earth and Planetary Science Letters* **79**, 397–411.
- Connolly, J. A. D. (2017). A primer in Gibbs energy minimization for geophysicists. *Petrology* **25**, 526–534.
- Darken, L. S. (1948). Melting points of iron oxides on silica; Phase equilibria in the system  $Fe$ – $Si$ – $O$  as a function of gas composition and temperature. *Journal of the American Chemical Society* **70**, 2046–2053.
- Darken, L. S. & Gurry, R. W. (1945). The system iron–oxygen. I. The wüstite field and related equilibria. *Journal of the American Chemical Society* **67**, 1398–1412.
- Ernst, W. G. (1960). The stability relations of magnesioriebeckite. *Geochimica et Cosmochimica Acta* **19**, 10–40.
- Eugster, H. P. (1957). Heterogeneous reactions involving oxidation and reduction at high pressures and temperatures. *The Journal of Chemical Physics* **26**, 1760–1761.
- Eugster, H. P. (1959). Reduction and oxidation in metamorphism. In: Abelson, P. H. (ed.) *Researches in Geochemistry*. New York: Wiley, p. 511.
- Eugster, H. P. & Wones, D. R. (1962). Stability relations of the ferruginous biotite, annite. *Journal of Petrology* **3**, 82–125.
- Foley, S. F. (2011). A reappraisal of redox melting in the Earth's mantle as a function of tectonic setting and time. *Journal of Petrology* **52**, 1363–1391.
- Frost, B. R. (1991). Introduction to oxygen fugacity and its petrologic importance. *Reviews in Mineralogy and Geochemistry* **25**, 1–9.
- Frost, D. J. & McCammon, C. A. (2008). The redox state of Earth's mantle. *Annual Review of Earth and Planetary Sciences* **36**, 389–420.
- Gaetani, G. A. (2016). The behavior of  $Fe^{3+}/\Sigma Fe$  during partial melting of spinel lherzolite. *Geochimica et Cosmochimica Acta* **185**, 64–77.
- Ganguly, J. (2005). Adiabatic decompression and melting of mantle rocks: An irreversible thermodynamic analysis. *Geophysical Research Letters* **32**.
- Ghiorso, M. S. & Evans, B. W. (2008). Thermodynamics of rhombohedral oxide solid solutions and a revision of the Fe–Ti two-oxide geothermometer and oxygen–barometer. *American Journal of Science* **308**, 957–1039.
- Giggenbach, W. F. (1992). Magma degassing and mineral deposition in hydrothermal systems along convergent plate boundaries. *Economic Geology* **87**, 1927–1944.

- Giuli, G., Alonso-Mori, R., Cicconi, M. R., Paris, E., Glatzel, P., Eeckhout, S. G. & Scaillet, B. (2012). Effect of alkalis on the Fe oxidation state and local environment in peralkaline rhyolitic glasses. *American Mineralogist* **97**, 468–475.
- Haggerty, S. E. (1976). Oxidation of opaque mineral oxides in basalts. *Reviews in Mineralogy and Geochemistry* **3**, Hg-1–Hg-100.
- Li, W., Cheng, Y. & Yang, Z. (2019). Geo- $fO_2$ : Integrated software for analysis of magmatic oxygen fugacity. *Geochemistry, Geophysics, Geosystems* **20**, 2542–2555.
- Lindsley, D. H. (1976). Experimental studies of oxide minerals. *Reviews in Mineralogy and Geochemistry* **3**, L-61–L-88.
- Marks, M. A. W., Schilling, J., Coulson, I. M., Wenzel, T. & Markl, G. (2008). The alkaline–peralkaline Tamazeght Complex, High Atlas Mountains, Morocco: Mineral chemistry and petrological constraints for derivation from a compositionally heterogeneous mantle source. *Journal of Petrology* **49**, 1097–1131.
- McKenzie, D. & Bickle, M. J. (1988). The volume and composition of melt generated by extension of the lithosphere. *Journal of Petrology* **29**, 625–679.
- Muan, A. (1955). Phase equilibria in the system FeO–Fe<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>. *JOM* **7**, 965–976.
- O'Neill, H. S. C. (1987). Quartz–fayalite–iron and quartz–fayalite–magnetite equilibria and the free energy of formation of fayalite (Fe<sub>2</sub>SiO<sub>4</sub>) and magnetite (Fe<sub>3</sub>O<sub>4</sub>). *American Mineralogist* **72**, 67–75.
- O'Neill, H. S. C., Berry, A. J. & Mallmann, G. (2018). The oxidation state of iron in Mid-Ocean Ridge Basaltic (MORB) glasses: Implications for their petrogenesis and oxygen fugacities. *Earth and Planetary Science Letters* **504**, 152–162.
- O'Neill, H. S. C., Berry, A. J., McCammon, C. C., Jayasuriya, K. D., Campbell, S. J. & Foran, G. (2006). An experimental determination of the effect of pressure on the Fe<sup>3+</sup>/ΣFe ratio of an anhydrous silicate melt to 3.0 GPa. *American Mineralogist* **91**, 404–412.
- O'Neill, H. S. C. & Wall, V. J. (1987). The olivine–orthopyroxene–spinel oxygen geobarometer, the nickel precipitation curve, and the oxygen fugacity of the Earth's upper mantle. *Journal of Petrology* **28**, 1169–1191.
- Ohmoto, H. & Kerrick, D. M. (1977). Devolatilization equilibria in graphitic systems. *American Journal of Science* **277**, 1013–1044.
- Roedder, E. (1951). Low temperature liquid immiscibility in the system K<sub>2</sub>O–FeO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>. *American Mineralogist* **36**, 282–286.
- Scaillet, B. & Evans, B. W. (1999). The 15 June 1991 eruption of Mount Pinatubo. I. Phase equilibria and pre-eruption  $P$ – $T$ – $fO_2$ – $fH_2O$  conditions of the dacite magma. *Journal of Petrology* **40**, 381–411.
- Xu, C., Campbell, I. H., Allen, C. M., Huang, Z., Qi, L., Zhang, H. & Zhang, G. (2007). Flat rare earth element patterns as an indicator of cumulate processes in the Lesser Qinling carbonatites, China. *Lithos* **95**, 267–278.
- Zaitsev, A. N., Marks, M. A. W., Wenzel, T., Spratt, J., Sharygin, V. V., Strekopytov, S. & Markl, G. (2012). Mineralogy, geochemistry and petrology of the phonolitic to nephelinitic Sadiman volcano, Crater Highlands, Tanzania. *Lithos* **152**, 66–83.





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