Earth science

Role of fO_2 on fluid saturation in oceanic basalt

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Assessing the conditions under which magmas become fluid-saturated has important bearings on the geochemical modelling of magmas because volatile exsolution may profoundly alter the behaviour of certain trace elements that are strongly partitioned in the coexisting fluid[1]. Saal *et al.*[2] report primitive melt inclusions from dredged oceanic basalts of the Siqueiros transform fault, from which they derive volatile abundances of the depleted mantle, based on the demonstration that magmas are not fluid-saturated at their eruption depth and so preserve the mantle signature in terms of their volatile contents. However, in their analysis, Saal *et al.*[2] consider only fluid–melt equilibria, and do not take into account the homogeneous equilibria between fluid species, which, as we show here, may lead to a significant underestimation of the pressure depth of fluid saturation.

For any basalt melt that is at fixed temperature and pressure in fluid-saturated conditions with known H_2O and CO_2 concentrations, the corresponding volatile fugacities, fH_2O and fCO_2, can be calculated[3]. The phase rule states that this in turn fixes the fugacities of all other C–O–H fluid species, including fO_2 (ref. 4). Figure 1a shows the covariation of the mole fraction of H_2O and CO_2 (XH_2O and XCO_2) in a C–O–H fluid calculated for various fO_2 at 1,200 °C and 400 bar (fO_2 expressed in log units relative to the solid buffer Ni–NiO, referred to here as NNO). It can be seen that at a very low mole fraction of H_2O ($XH_2O < 0.05$), reduced fluids are poorer in CO_2 than oxidized ones: for instance, at $\Delta NNO = -2$ the mole fraction of CO_2 is 0.8, whereas at $\Delta NNO = -0.8$, it is 0.95. This is due to the progressive reduction of CO_2 into CO, which becomes significant at fO_2 below $\Delta NNO = -1$ (ref. 4).

Figure 1b shows the H_2O and CO_2 concentrations of basalt melts that coexist with fluids shown in Fig. 1a. Under oxidizing conditions ($fO_2 > \Delta NNO = -1$), the overall shape of the curve resembles the pattern of the curve when it is calculated by considering only fluid–melt equilibria[2]. By contrast, for $fO_2 < \Delta NNO = -1$, the isobaric curve displays an asymmetric bell-shaped pattern characterized by a strong lowering of the melt CO_2 content at low H_2O. As already stated, this is the result of the reduction of CO_2 to CO at low fO_2, CO being an insoluble species in silicate melts at low pressures[5]. The two curves merge at melt H_2O contents higher than 1 wt%, which shows that, for basalt melts with a higher meltwater content, the calculation of pressure for fluid saturation in the C–O–H system does not require an accurate knowledge of their redox state — unlike H_2O-poor basalts, such as oceanic basalts[2].

The fO_2 of primitive melt inclusions at Siqueiros is at present not well constrained but is estimated to be around $\Delta NNO = -2$ (ref. 2), which would fall at the upper end of the range of fO_2 estimated for mid-ocean-ridge basalt[6] (MORB). However, given the general inverse correlation between fO_2 and MgO of MORB documented worldwide[6], the Siqueiros magmas would be expected near the lower end of the range (that is, $\Delta NNO = -3.5$; ref. 6). The CO_2 contents of Siqueiros melt inclusions average at 132 ± 34 p.p.m. but range from 43 p.p.m. up to 243 p.p.m. (ref. 2).

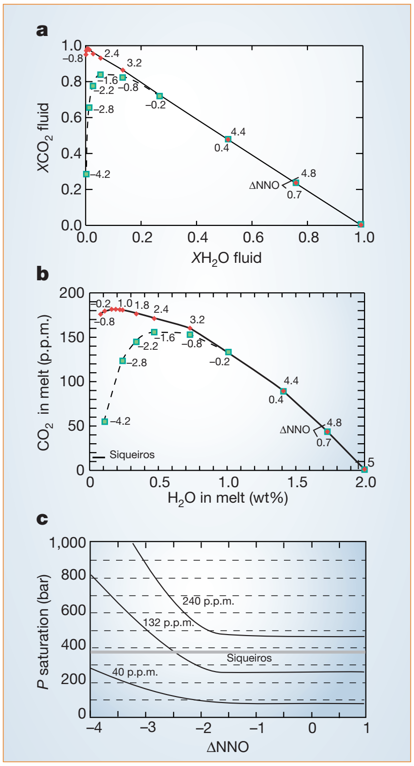

Figure 1 Effect of fO_2 on fluid speciation and fluid saturation in basalts. **a,** Covariation of XH_2O and XCO_2 (where Xi is the mole fraction of species *i*) in a C–O–H fluid calculated for various values of fO_2 (numbers along each curve). The calculations were done by fixing fH_2 (either 0.01 bar or 1 bar, corresponding to red and green symbols, respectively) and fH_2O, which allows us to calculate fCO_2 in the C–O–H system[4]. Once fH_2 and fH_2O are fixed, fO_2 can be calculated through the equilibrium $H_2 + 0.5\,O_2 = H_2O$. *T*, 1,200 °C; *P*, 400 bar. **b,** H_2O–CO_2 solubility diagram for a basalt at 1,200 °C and 400 bar and equilibrated with fluid compositions shown in **a**. For any given fH_2O and fCO_2 set of values, the corresponding H_2O and CO_2 contents of the melt are computed according to ref. 3. The fO_2 is shown along each line in log units calculated relative to the solid buffer Ni–NiO. The Siqueiros bar shows the range of H_2O content of Siqueiros melt determined by Saal *et al.*[2]. **c,** Evolution of the pressure of fluid saturation with fO_2 of a basalt melt having 40, 132 and 240 p.p.m. CO_2 and 0.1 wt% H_2O, which are minimum, average and maximum CO_2 contents, respectively, of the Siqueiros melt inclusions[2]. At an fO_2 below $\Delta NNO = -1$, the pressure of saturation in fluid rises because of the continuous increase in CO of the coexisting gas phase. Grey horizontal line corresponds to the average collection pressure of Siqueiros basalts.

Figure 1c shows the evolution of the pressure of fluid saturation with fO_2 of basalt melts having 40, 132 and 240 p.p.m. CO_2 and 0.1 wt% H_2O. It can be seen that, except for the lowest CO_2 contents, most melts would be fluid-saturated at their collection pressure for an $fO_2 < \Delta NNO = -2.5$. Considering the uncertainties associated with the determination of dissolved CO_2 in MORB glasses (± 15 p.p.m.) and with the redox state of Siqueiros magmas, we contend that the condition of fluid saturation before eruption cannot be disregarded for at least the most CO_2-rich Siqueiros melt inclusions.

We note that this condition is in agreement with earlier findings showing that the redox state of oceanic basalts is compatible with mantle melting under fluid-present or graphite-saturated conditions[7,8]. Therefore, although the variable CO_2 content of quenched oceanic basaltic glasses results from syneruptive degassing[3], part of this variability may also reflect regional-to-local variations in fO_2. In general, a quantitative modelling of volatiles' behaviour in MORB magmas will require explicit consideration of the role of fO_2 (ref. 9).

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Saal et al. *reply* — Scaillet and Pichavant[1] raise an important point about the role that fO_2 plays in determining C–H–O fluid speciation and in estimating the degree of vapour saturation in oceanic basalts. However, this does not seem to be relevant to the volatile geochemistry of mid-ocean-ridge basalt (MORB) magmas in general and of Siqueiros MORB in particular.

To address their comments, we should first mention that the compositions of the Siqueiros picritic glasses are representative of MORB. Their primitive composition does not indicate an unusually large extent of depletion compared with normal MORB, and indicates that they were not affected by the pervasive fractionation, mixing and aggregation processes taking place at the centre of the ridge segments[2–4].

The key factor in Scaillet and Pichavant's comment is the fO_2 of MORB. The authors incorrectly suggest that the Saal *et al.*[4] estimation of the fO_2 of Siqueiros lavas falls at the upper range of the fO_2 estimated for MORB. Saal *et al.*[4] calculated the fO_2 for Siqueiros picritic glasses and melt inclusions as $\Delta NNO = -1.7 \pm 0.5$ (2σ), using the compositions of syngenetic chromium–spinel inclusions in olivine phenochrysts[5]. The fO_2 value for Siqueiros samples agrees very well with previous estimations of the fO_2 for MORB, ranging from $\Delta NNO = -2.10 \pm 95$ (2σ) (ref. 6) to $\Delta NNO = -1.32 \pm 0.86$ (2σ) (ref. 7).

Our estimate of the fO_2 for Siqueiros samples, $\Delta NNO = -1.75$, is therefore a conservative value. Under these conditions ($\Delta NNO \geqslant -2$), the amount of CO existing with CO_2 is negligible (Fig. 1c of ref. 1). Furthermore, Scaillet and Pichavant[1] estimate an fO_2 of $\Delta NNO = -3.5$ for the Siqueiros samples, invoking a global correlation between $Fe^{+3}/\Sigma Fe$ ratios and MgO content in MORB[6]. However, the existing data[6,7] show no clear correlation, but variation in $Fe^{+3}/\Sigma Fe$ ratios from 0.02 to 0.06 at any given MgO content.

The conclusions of Scaillet and Pichavant[1] also depend critically on the fugacity of molecular hydrogen (fH_2) in MORB and their discussion relies on an estimate for a high fH_2 in MORB (1 bar at 400 bars total pressure). Their Fig. 1a shows that similar calculations made with a lower fH_2 result in no production of CO, and that the carbon speciation is dominated by CO_2. Measurements of the composition of fluids trapped in MORB vesicles show that reduced vapour species (CO, H_2, CH_4) are typically less than 0.03–1 vol% of the total vapour, even at low water content[8,9]. These measurements point to the very low abundance of reduced C–H species in the fluids that are in equilibrium with MORB, and indicate that the estimates of vapour-saturation pressure in Siqueiros MORB (and indeed, probably all MORB) are accurate.

Several other observations have not been addressed by Scaillet and Pichavant. First, their estimated vapour-saturation pressures at fO_2 $\Delta NNO < -2$ (Fig. 1c of ref. 1) assume a finite solubility for CO in basaltic melt, but in fact the solubility of CO in basalt has not been directly measured. As a result, even if a basaltic melt did have a significant CO content, it is not yet possible accurately to estimate the vapour-saturation pressure of basalt in the presence of a mixed CO–CO_2 fluid[10,11].

Second, if vapour exsolution from the Siqueiros magmas had been important, we would expect that lavas that underwent degassing would contain a large amount of vesicles. However, the very low (0–0.5 vol%) vesicularity of the Siqueiros host glasses is consistent with their range from nearly saturated to undersaturated in H_2O–CO_2 vapour at the pressure of eruption[4].

Third, significant degassing of CO would have destroyed the observed correlation between CO_2, Nb and Cl contents in the Siqueiros samples[4]. CO_2–Nb–Cl correlations are very difficult to explain if degassing of CO was important in those samples. Furthermore, Siqueiros melt inclusions and host glasses have the highest CO_2/Nb ratios of all MORB analysed, even though MORB is generally supersaturated in H_2O–CO_2 at the depth of eruption (because the rate of cooling is faster than that of bubble nucleation)[4,12]. The simplest explanation for the CO_2–Nb–Cl correlation and the high CO_2/Nb ratios for the Siqueiros samples is that the picritic glasses and inclusions are undegassed.

Finally, it is clear that in the case of the Siqueiros melt inclusions they were trapped at pressures higher than the pressure of eruption of the lavas. Therefore the 400-bars pressure used by Saal *et al.*[4] is a minimum estimation of the pressure of entrapment. If the inclusions were trapped at a pressure higher than 400 bars, their dissolved volatile contents would be lower than those required to saturate a basaltic melt in H_2O–CO_2 vapour.

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