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Earth science: Role of fO_2 on fluid saturation in oceanic basalt

[Brief Communications Arising]

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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 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.

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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).

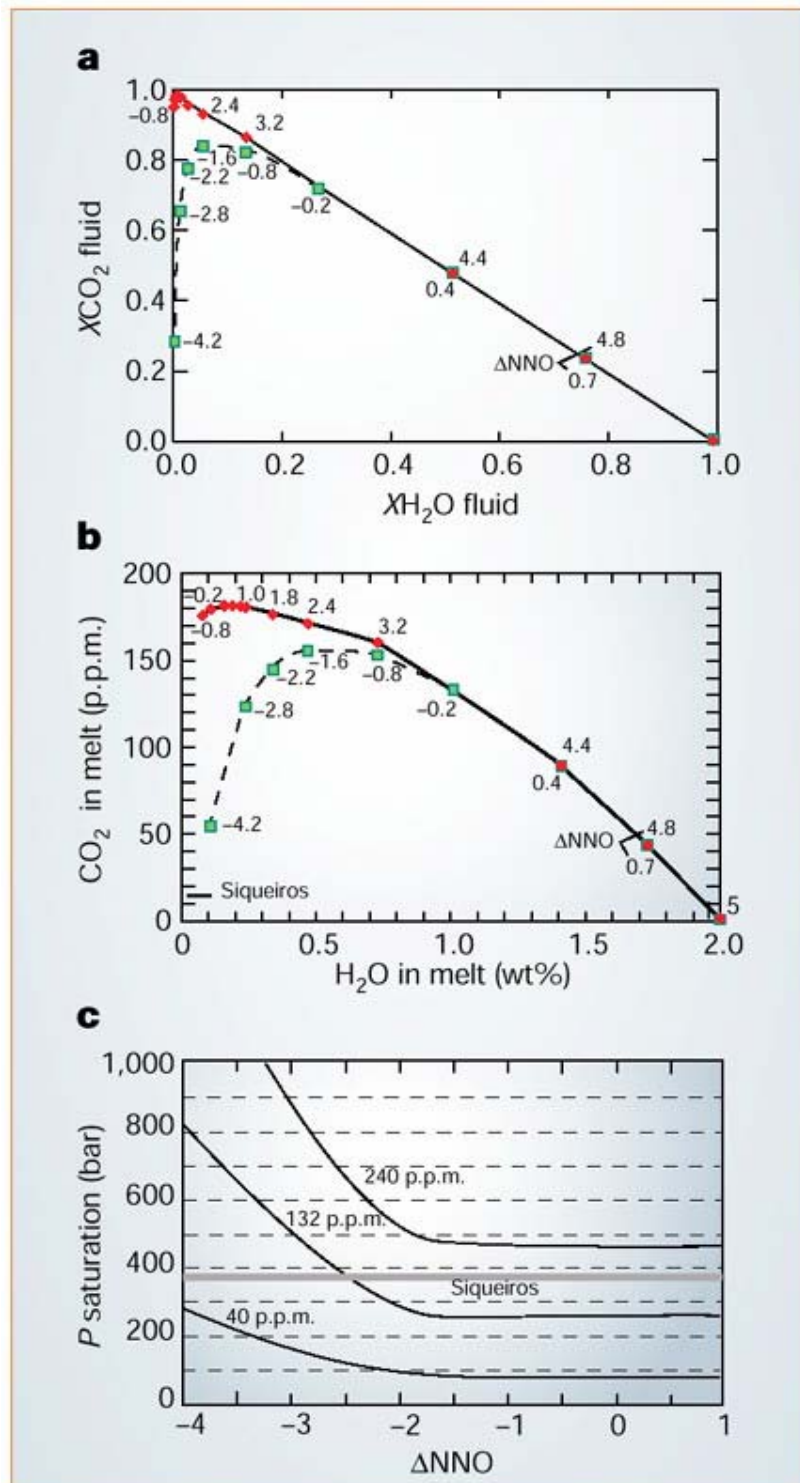


Figure 1 Effect of f_{O_2} on fluid speciation and fluid saturation in basalts. a, Covariation of X_{H_2O} and X_{CO_2} (where X_i is the mole fraction of species i) in a C-O-H fluid calculated for various values of f_{O_2} (numbers along each curve). The calculations were done by fixing f_{H_2} (either 0.01 bar or 1 bar, corresponding to red and green symbols, respectively) and f_{H_2O} , which allows us to calculate f_{CO_2} in the C-O-H system 4. Once f_{H_2} and f_{H_2O} are fixed, f_{O_2} can be calculated through the equilibrium $H_2 + 0.5 O_2 = H_2O$. T, 1,200 °C; P, 400 bar. b, H₂O-CO₂ solubility diagram for a basalt at 1,200 °C and 400 bar and equilibrated with fluid compositions shown in a. For any given f_{H_2O} and f_{CO_2} set of values, the corresponding H₂O and CO₂ contents of the melt are computed according to ref. 3. The f_{O_2} is shown along each line in log units calculated relative to the solid buffer Ni-NiO. The Siqueiros bar shows the range of H₂O content of Siqueiros melt determined by Saal et al. 2. c, Evolution of the pressure of fluid saturation with f_{O_2} of a basalt melt having 40, 132 and 240 p.p.m. CO₂ and 0.1 wt% H₂O, which are minimum, average and maximum CO₂ contents, respectively, of the Siqueiros melt inclusions 2. At an f_{O_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.