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LETTERS

The redox state of Pinatubo dacite and the ilmenite-hematite solvus

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ABSTRACT

The oxidation state of the 1991 Pinatubo dacite and many other oxidized silicic arc volcanic rocks has been overestimated. We reproduce the compositions of magnetite and ferrian ilmenite found in Pinatubo dacite by doing crystallization experiments at 780 °C, 2.2 kbar, and NNO + 1.7 (±0.2) log units. The extra components in igneous ilmenite, notably geikielite, expand the solvus in a way that is not correctly accomodated in current formulations of the iron titanium oxide thermobarometer.

INTRODUCTION

Knowledge of the redox state, or oxygen fugacity (f_{O_2}), of a magma is of great importance to igneous petrogenesis. Oxygen fugacity exerts a first-order control on fractionation paths, and it may reflect the redox state of the magma's source, or alternatively point to open-system processes such as magma mixing, contamination, volatile flushing, or extended crystal fractionation. An accurate estimate of the f_{O_2} of a magma thus provides a valuable constraint on models of its evolution. As a chemical species, O_2 participates in homogeneous gas equilibria that connect the fugacities of other gas species, including major ones like H_2O, CO_2, H_2S, SO_2 (e.g., Westrich and Gerlach 1992; Matthews et al. 1994), and it is a determining variable in the solubility of S in magmas (Carroll and Rutherford 1987). Thus, the magnitude of f_{O_2} has much relevance to issues of gas saturation in magmas, volcanic hazards, and climatic effects.

One of petrology's most successful mineral thermobarometers has been that based on the compositions of coexisting iron titanium oxides in quenched volcanic rocks. It has been well calibrated by experimental phase equilibrium, order-disorder, and calorimetric measurements at high temperature in the range of f_{O_2} from the solid buffer wüstite-magnetite (WM) to that of nickel-nickel oxide (NNO) (Buddington and Lindsley 1964; Spencer and Lindsley 1981; Andersen and Lindsley 1988). Few experimental calibrations have been performed at f_{O_2} greater than NNO, and application of the thermobarometer is generally understood to be increasingly unreliable the more f_{O_2} rises above NNO. Lindsley and Frost (1992), for example, caution users to beware of calculations above fayalite-magnetite-quartz (FMQ) + 2 log units (~NNO + 1.3). It has nevertheless been used in this range in numerous petrological studies, in particular on intermediate and silicic, typically H_2O-rich volcanic rocks in orogenic arcs. In principle, formulations of the thermobarometer rigorously based on thermodynamics (e.g., Ghiorso and Sack 1991) should permit a reasonable degree of extrapolation to *P*, *T*, and f_{O_2} conditions outside the calibrated range.

COMPARATIVE ESTIMATES OF REDOX STATE

At equilibrium at a known temperature with liquid, the compositions (mg no.) of olivine, orthopyroxene, and cummingtonite provide upper limits to possible values of f_{O_2} (or, with quartz and iron titanium oxides, actual values of f_{O_2}) based on redox equilibria with the oxides (Lindsley and Frost 1992; Frost and Lindsley 1992). Evans and Ghiorso (1995, Fig. 10) compared the computed temperature, relative f_{O_2}, and composition of cummingtonite with values for these same variables derived from measured compositions of cummingtonite and iron titanium oxide phenocrysts in dacites and rhyolites containing orthopyroxene and quartz. Up to a value of f_{O_2} corresponding to NNO + 1 log unit, agreement was found to be excellent. Above NNO + 1, the composition of cummingtonite indicated more reducing conditions than the iron titanium oxide barometer, and oxide temperatures exceeded by several tens of degrees, those possible for cummingtonite (maximum ~790 °C, Geschwind and Rutherford 1992; Evans and Ghiorso 1995). The cummingtonite-bearing dacites of St. Helens (layer Y) and the 1991 eruption of Pinatubo Volcano were notable examples of the disagreement.

For the 1991 Pinatubo dacite, estimates of f_{O_2} in the literature, based on diverse O_2 "barometers" (mostly accompanied by appropriate caveats) have ranged from

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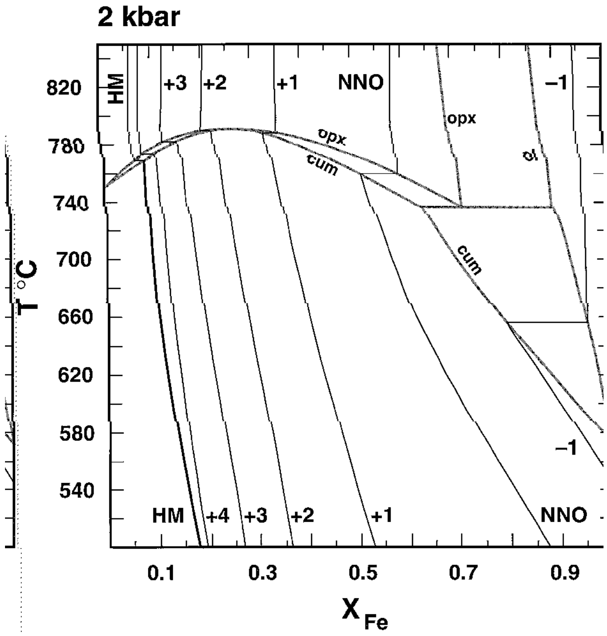

FIGURE 1. Calculated T-X_{Fe} diagram at 2 kbar for the redox and other equilibria in the system Fe-MgO-SiO$_2$-H$_2$O-O of cummingtonite, orthopyroxene, and olivine, with reference to log f_{O_2} defined by the NNO buffer, from Evans and Ghiorso (1995).

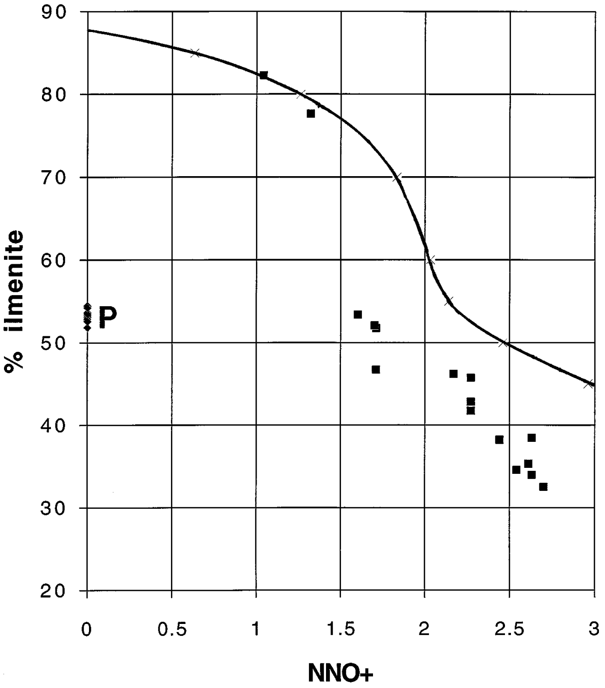

FIGURE 2. Compositions of rhombohedral coexisting with cubic iron titanium oxide in experiments on fused Pinatubo dacite at 780 °C, 2.2 kbar, and controlled f_{O_2} (filled squares). Isotherm for 780 °C from Ghiorso and Sack (1991). P is composition of ferrian ilmenite in natural Pinatubo dacite.

NNO + 2 to near or even equal to hematite-magnetite (HM) (which is NNO + 4.7 at 2 kbar and 780 °C), with apparently a consensus at about NNO + 3 (Bernard et al. 1991; Pallister et al. 1992, 1996; Imai et al. 1993; Hattori 1993; Rutherford and Devine 1996; Fournelle et al. 1996). The iron titanium oxide thermobarometer gave NNO + 2.3 to 2.6 according to the Ghiorso and Sack (1991) calibration and NNO + 2.3 to 3.0 according to the Andersen and Lindsley (1988) calibration as applied by Matthews et al. (1992), Hattori (1993), and Rutherford and Devine (1996). We estimate NNO $\leq$ + 1.6 based on the molar percent of Fe end-member of the cummingtonite (0.29) and the data of Evans and Ghiorso (1995; Fig. 1 here), with allowance for Fe^{3+} and Al in the cummingtonite. Rare, non-xenocrystic orthopyroxene in the dacite has a comparable composition: 0.29 and 0.28 mol% Fe end-member (Matthews et al. 1992; Imai et al. 1993) and thus provides the same constraint on f_{O_2} as the cummingtonite (Fig. 1).

EXPERIMENTAL RESULTS

On the basis of experiments conducted at the CNRS laboratory, Orléans, we conclude that the reason for the disagreement between silicate and oxide O$_2$ barometers is use of the latter at redox states more oxidizing than NNO + 1. Hydrothermal experiments of two to three weeks duration were performed at 2.2 kilobars, 780 ± 5 °C, and redox states controlled by the use of cold-seal and internally heated vessels equipped with the Shaw membrane (Scaillet et al. 1992) for the control of f_{H_2}. A Ni-Pd sensor for f_{O_2} was used in several experiments, giving excellent agreement with the f_{O_2} based on the measured H$_2$ and H$_2$O pressures. The compositions of ferrian ilmenite and titanian magnetite in the natural Pinatubo dacite were reproduced in experiments on previously fused and ground Pinatubo dacite at NNO + 1.6 and NNO + 1.7. In experiments on unfused Pinatubo dacite at NNO + 2.5 and the same P and T conditions, the natural magnetite largely altered to a more Ti-poor composition, and the ferrian ilmenite grew more Ti-poor rims. The composition of the rhombohedral phase coexisting with titanian magnetite at 780 ± 5 °C as a function of experimental f_{O_2} are shown in Figure 2, with the calibration of Ghiorso and Sack (1991) for the binary system Fe-Ti-O at 780 °C for comparison. For consistency, we project the complex oxides to the binary join using their procedure, namely X_{ilm} = ilm/(ilm + hem + cor). Agreement is good at NNO + 1.0 but poor above NNO + 1.5, with the experiments suggesting a much steeper dX_{ilm}/dlog f_{O_2} slope in this range. The calibration of Andersen and Lindsley (1988) shows the same progressive departure from the experiments with increase in f_{O_2}. It should be noted that Rutherford and Devine (1996) used the Re-ReO$_2$ O$_2$ buffer to obtain their best fit to the compositions of the Pinatubo

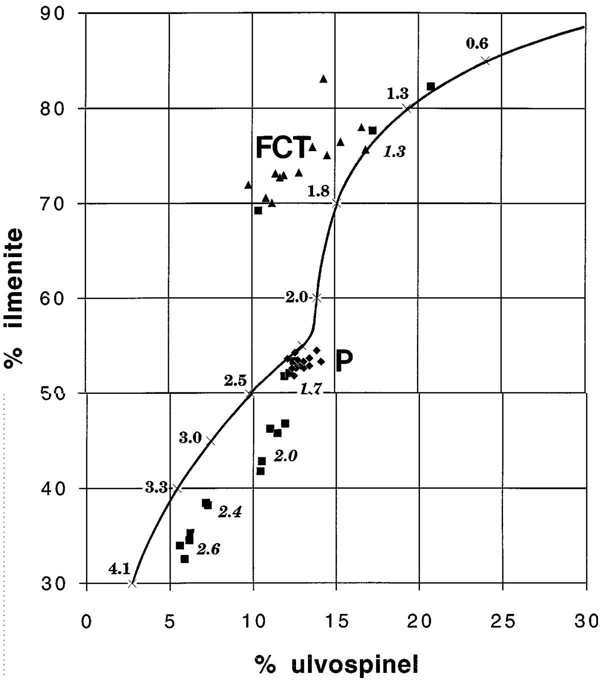

FIGURE 3. Roozeboom plot of coexisting rhombohedral and cubic iron titanium oxides (filled squares) in experiments on fused Pinatubo dacite at 780 °C and 2.2 kbar, with f_{O_2} as NNO+ in italics. Natural pairs from Pinatubo dacite (P and diamonds) and Fish Canyon Tuff (FCT and triangles) for comparison. Three of the 16 FCT oxide pairs were deleted according to the Bacon and Hirschmann (1988) criteria. Isotherm for 780 °C from Ghiorso and Sack (1991), with NNO+ values.

iron titanium oxides and the residual melt at 780 °C, and the calculated f_{O_2} of this buffer is approximately NNO + 2.

Construction of a Roozeboom diagram (Fig. 3) helps illuminate the differences between the experimental results on the multicomponent oxides in Pinatubo dacite and the calibration of Ghiorso and Sack (1991) for the pure iron titanium oxides. This diagram does not require knowledge of f_{O_2}, although it can be contoured for relative values of f_{O_2} (e.g., Ghiorso and Sack 1991, Fig. 5). Added to the diagram are the compositions of coexisting iron titanium oxide minerals in the natural Pinatubo dacite (Imai et al. 1993; Hattori 1993; Pallister et al. 1996; Rutherford and Devine 1996) and the Fish Canyon Tuff (Stormer and Whitney 1985; Whitney and Stormer 1985). On the basis of experimental phase equilibrium and phase composition data, the pre-eruption temperatures of these magmas are believed to have been 780 and 760 °C, respectively (Johnson and Rutherford 1988; Pallister et al. 1992, 1996; Rutherford and Devine 1996). Note that the trend of experimental data passes through the data-set for Pinatubo. This lends support to the belief that the experimental data represent equilibrium compositions; although the experimental products were obtained by synthesis from powdered glass, the charges were saturated in H_2O-rich fluid, and this technique has worked well for silicic compositions (Scaillet et al. 1995). Mg and Mn are partitioned according to the equilibrium model of Bacon and Hirschmann (1988). Given the temperature, experimental duration, and grain size (typically ≤ 10 micrometers), reasonably equilibrated iron titanium oxides are consistent with what we know about their reaction kinetics (Hammond and Taylor 1982; Nakamura 1995). Note also that the trend for the Fish Canyon Tuff (FCT) diverges from the 780 °C model isotherm, but that X_{usp} in FCT samples overlaps those for Pinatubo and our experiments at NNO + 1.6 to 1.7 in spite of a large difference in X_{ilm} (53 cf. 70). The logical conclusion is that the natural oxide and 780 °C experimental pairs formed at subsolvus conditions, whereas the model curve is supersolvus. The tricritical point (solvus crest) in the pure hematite-ilmenite system, based on an analysis of all available data (Ghiorso 1990), is at 760 °C and 57% ilmenite. Note that one experimental charge (with added S) produced a geikielite-rich (12%) ilm_{69} and usp_{10} in the same vessel (i.e., same *P*, *T*, and f_{O_2}) as others that produced ilm_{43} and usp_{10}. We did not find a solvus pair within one charge, however. The zoned ferrian ilmenite from a Pinatubo dacite described by Hoffman and Fehr (1996), $ilm_{56.4}$ core to $ilm_{50.9}$ rim (using our projection scheme), encompasses the compositions of all analyzed ferrian ilmenites in Pinatubo dacite (Fig. 3) and does not span the solvus.

As befits their location to the left (lower temperature) side of the 780 °C isotherm in Figure 3, the FCT samples give oxide temperatures of 706 to 771 °C (average 738 °C) according to Andersen and Lindsley (1988) and 671 to 796 °C (average 744 °C) according to Ghiorso and Sack (1991, Table 1). These temperatures are slightly low with respect to inferred pre-eruption conditions based on phase equilibrium arguments (Johnson and Rutherford 1988). On the other hand, the temperatures that we would calculate from the compositions of the iron titanium oxides in our more oxidizing experiments using the Ghiorso and Sack (1991) formulation are too high (right side of 780 °C isotherm in Fig. 3) and in fact rise from 800 °C to in excess of 1000 °C toward increasing applied f_{O_2}. From the theoretical formulation we also recover values of relative f_{O_2} that range up to several orders of magnitude too high for the most oxidizing experiments. These extreme results are correlated errors due, in graphical terms, to the acute intersections of compositional isopleths in the conventional thermobaric diagram at high f_{O_2}, where the composition of the rhombohedral oxide is on the disordered, hematite-rich side of the $R\bar{3}$-$R\bar{3}c$ transition in the T-X_{ilm} phase diagram.

CONCLUSIONS

Why then do we recover very satisfactory temperatures and oxygen fugacities using the iron titanium oxides in the f_{O_2} range up to ~NNO+ 1 but not beyond? This limit does not correspond to a major increase in the content of impurity components (e.g., Mg, Mn, Al), which might serve to magnify the projection problem or their nonideal thermodynamic effects. On the other hand, the higher f_{O_2} brings us to the vicinity of the binary rhombohedral solvus, where small variations in the activities of the $FeTiO_3$ and Fe_2O_3 components correspond to large variations in composition (X_{ilm}). Here, dramatic compositional errors are possible if the thermodynamic effects of additional components, such as geikielite ($MgTiO_3$), pyrophanite ($MnTiO_3$), and corundum (Al_2O_3), are not properly accounted for. Of these possibilities, the geikielite component in the present case is the most likely culprit because it is present, for example, at the 4 to 5% level in the ferrian ilmenite in the Pinatubo dacite, as compared with 0.5% for both pyrophanite and corundum. Ghiorso and Sack (1991, p. 486) recognized this issue as a major difficulty in modeling the thermobarometer. In the absence of data on the geikielite-hematite join, Ghiorso (1990) adopted model ordering parameters equivalent to those for the ilmenite-hematite join. In retrospect, one might have predicted greater immiscibility on the geikielite-hematite join, and this is probably what our data at 780 °C and the FCT and Pinatubo data within the complex natural system are indicating. If the ilmenite-hematite solvus widens with increasing geikielite content, then there is no unique field for two natural rhombohedral phases in a projection like Figure 3.

We believe that the iron titanium oxide thermobarometer is not yet ready for application to oxidized arc volcanics at temperatures on the order of 800 °C or less. Temperatures extracted will be low or high depending on the compositional range of the ilmenite, and the f_{O_2} will be too high. Several examples of ilmenite with compositions in the ‘‘danger’’ zone of the solvus, aside from those already mentioned, may be found in volcanic rocks in western North and South America (e.g., Carmichael 1967; Lipman 1971; Rose et al. 1979; Heiken and Eichelberger 1980; Smith and Leeman 1982; Feeley and Davidson 1994). For the Pinatubo dacite, we suggest that the pre-eruption redox state was somewhere between NNO + 1.4 and NNO + 2.0. Plutonic and metamorphic rocks with primary ilmenite falling in the same compositional range will also be problematic for the same reason. Especially helpful in formulating a revision of the thermobarometer for these conditions would be experimental work on the solvus in the hematite-geikielite system and experiments crystallizing iron titanium oxide pairs at known *T*, *P*, and high f_{O_2} in variably Ti-, Mg-, and Fe-doped, H_2O-saturated rhyolite glass.

We have not addressed the question of how the high oxidation state of silicic arc magmas such as the Pinatubo dacite is reached, but we suggest that the magnitude of the problem is less than previously thought. The impact of our correction on calculations of gas compositions (Westrich and Gerlach 1992) is not trivial; an adjustment in relative f_{O_2} from NNO + 3 to NNO + 1.5, for example, changes the calculated ratio SO_2/H_2S in the gas phase by 2.25 log units, or a factor of 178.

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REFERENCES CITED

Andersen, D.J. and Lindsley, D.H. (1988) Internally consistent solution models for Fe-Mg-Mn-Ti oxides: Fe-Ti oxides. American Mineralogist, 73, 714–726.

Bacon, C.R. and Hirschmann, M.M. (1988) Mg/Mn partitioning as a test for equilibrium between coexisting Fe-Ti oxides. American Mineralogist, 73, 57–61.

Bernard, A., Demaiffe, D., Mattielli, N., and Punongbayan, R.S. (1991) Anhydrite-bearing pumices from Mount Pinatubo: further evidence for the existence of sulphur-rich silicic magmas. Nature, 354, 139–140.

Buddington, A.F. and Lindsley, D.H. (1964) Iron-titanium oxide minerals and synthetic equivalents. Journal of Petrology, 5, 310–357.

Carmichael, I.S.E. (1967) The iron-titanium oxides of salic volcanic rocks and their associated ferromagnesian silicates. Contributions to Mineralogy and Petrology, 14, 36–64.

Carroll, M.R. and Rutherford, M.J. (1987) The stability of igneous anhydrite: experimental results and implications for sulfur behavior in the 1982 El Chichon trachyandesite and other evolved magmas. Journal of Petrology, 28, 781–801.

Evans, B.W. and Ghiorso, M.S. (1995) Thermodynamics and petrology of cummingtonite. American Mineralogist, 80, 649–663.

Feeley, T.C. and Davidson, J.P. (1994) Petrology of calc-alkaline lavas at Volcán Ollagüe and the origin of compositional diversity at central Andean stratovolcanoes. Journal of Petrology, 35, 1295–1340.

Fournelle, J., Carmody, R., and Daag, A.S. (1996) Anhydrite-bearing pumices from the June 15, 1991, eruption of Mount Pinatubo: geochemistry, mineralogy, and petrology. In C.G. Newhall and R.S. Punongbayan, Eds., Fire and Mud: Eruptions and Lahars of Mount Pinatubo, Philippines, p. 845–863. PHIVOLCS/University of Washington Press, Seattle.

Frost, B.R. and Lindsley, D.H. (1992) Equilibria among Fe-Ti oxides, pyroxenes, olivine and quartz: Part II. Application. American Mineralogist, 77, 1004–1020.

Geschwind, C. and Rutherford, M.J. (1992) Cummingtonite and the evolution of the Mt. St. Helens (Washington) magma system.: An experimental study. Geology, 20, 1011–1014.

Ghiorso, M.S. (1990) Thermodynamic properties of hematite-ilmenite-geikielite solid solutions. Contributions to Mineralogy and Petrology, 104, 645–667.

Ghiorso, M.S. and Sack, R.O. (1991) Fe-Ti oxide geothermometry: thermodynamic formulation and the estimation of intensive variables in silicic magmas. Contributions to Mineralogy and Petrology, 108, 485–510.

Hammond, P.A. and Taylor, L.A. (1982) The ilmenite-titanomagnetite assemblage: kinetics of re-equilibration. Earth and Planetary Science Letters, 61, 143–150.

Hattori, K. (1993) High-sulfur magma, a product of fluid discharge from underlying mafic magma: evidence from Mount Pinatubo, Philippines. Geology, 21, 1083–1086.

——— (1996) Occurrence and origin of sulfide and sulfate in the 1991 Mount Pinatubo eruption products. In C.G. Newhall and R.S. Punongbayan, Eds., Fire and Mud: Eruptions and Lahars of Mount Pinatubo, Philippines, p. 807–824. PHIVOLCS and University of Washington Press, Seattle.

Heiken, G. and Eichelberger, J.C. (1980) Eruptions at Chaos Crags, Lassen Volcanic National Park, California. Journal of Volcanology and Geothermal Research, 7, 443–481.

Hoffman, V. and Fehr, K.T. (1996) Micromagnetic, rockmagnetic and mineralogical studies on dacite pumice from the Pinatubo eruption (1991, Philippines) showing self-reversed TRM. Geophysical Research Letters, 23, 2835–2838.

Imai, A., Listanco, E.L., and Fujii, T. (1993) Petrologic and sulfur isotopic significance of highly oxidised and sulfur-rich magma of Mt. Pinatubo, Philippines. Geology, 21, 699–702.

Johnson, M.C. and Rutherford, M.J. (1988) Experimentally determined conditions in the Fish Canyon Tuff, Colorado, magma chamber. Journal of Petrology, 30, 711–737.

Lindsley, D.H. and Frost, B.R. (1992) Equilibria among Fe-Ti oxides, pyroxenes, olivine, and quartz: Part I. Theory. American Mineralogist, 77, 987–1003.

Lipman, P.W. (1971) Iron-titanium oxide phenocrysts in compositionally zoned ash-flow sheets from Southern Nevada. Journal of Geology, 79, 438–456.

Matthews, S.J., Jones, A.P., and Bristow, C.S. (1992) A simple magma-mixing model for sulphur behaviour in calc-alkaline volcanic rocks: mineralogical evidence from Mount Pinatubo 1991 eruption. Journal of the Geological Society, London, 149, 863–866.

Matthews, S.J., Jones, A.P., and Beard, A.D. (1994) Buffering of melt oxygen fugacity by sulphur redox reactions in calc-alkaline magmas. Journal of the Geological Society, London, 151, 815–823.

Nakamura, M. (1995) Continuous mixing of crystal mush and replenished magma in the ongoing Unzen eruption. Geology, 23, 807–810.

Pallister, J.S., Hoblitt, R.P., and Reyes, A.G. (1992) A basalt trigger for the 1991 eruptions of Pinatubo volcano? Nature, 356, 426–428.

Pallister, J.S., Hoblitt, R.P., Meeker, G.P., Knight, R.J., and Siems, D.F. (1996) Magma mixing at Mount Pinatubo: petrographic and chemical evidence from the 1991 deposits. In C.G. Newhall and R.S. Punongbayan, Eds., Fire and Mud: Eruptions and Lahars of Mount Pinatubo, p. 687–731. PHIVOLCS and University of Washington Press, Seattle.

Rose, W.I. Jr., Grant, N.K., and Easter, J. (1979) Geochemistry of the Los Chocoyos ash, Quezaltenango Valley, Guatemala. Geological Society of America Special Paper, 180, 87–99.

Rutherford, M.J. and Devine, J.D. (1996) Preeruption pressure-temperature conditions and volatiles in the 1991 dacitic magma of Mount Pinatubo. In C.G. Newhall and R.S. Punongbayan, Eds., Fire and Mud: Eruptions and Lahars of Mount Pinatubo, Philippines, p. 751–766. PHIVOLCS and University of Washington Press, Seattle.

Scaillet, B., Pichavant, M., Roux, J., Humbert, G., and Lefèvre, A. (1992) Improvements of the Shaw membrane technique for measurement and control of f_{H_2} at high temperatures and pressures. American Mineralogist, 77, 647–655.

Scaillet, B., Pichavant, M., and Roux, J. (1995) Experimental crystallization of leucogranite magmas. Journal of Petrology, 36, 663–705.

Smith, D.R. and Leeman,W.P. (1982) Mineralogy and phase chemistry of Mt. St. Helens tephra sets W and Y as keys to their identification. Quaternary Research, 17, 211–227.

Spencer, K.J. and Lindsley, D.H. (1981) A solution model for coexisting iron-titanium oxides. American Mineralogist, 66, 1189–1201.

Stormer, J.C. Jr. and Whitney, J.A. (1985) Two-feldspar and iron-titanium oxide equilibria in silicic magmas and the depth of origin of large ash-low tuffs. American Mineralogist, 70, 52–64.

Westrich, H.R. and Gerlach, T.M. (1992) Magmatic gas source for the stratospheric SO_2 cloud from the June 15, 1991, eruption of Mount Pinatubo. Geology, 20, 867–870.

Whitney, J.A. and Stormer. J.C. Jr. (1985) Mineralogy, petrology and magmatic conditions from the Fish Canyon Tuff, central San Juan volcanic field, Colorado. Journal of Petrology, 26, 726–762.

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