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Ferric/ferrous ratios in 1984 Mauna Loa lavas: a contribution to understanding the oxidation state of Hawaiian magmas

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Abstract Ferric/ferrous ratios have been used to estimate the oxygen fugacity of lavas erupted in 1984 on Mauna Loa Volcano, Hawaii. Rapidly quenched lavas erupted close to vents are less oxidized than rapidly quenched lavas scooped from lava flows several kilometers away from the vents. These results demonstrate that sampling is of critical importance in determining the oxidation state of lava. The oxidation state of the vent lavas, below or at magnetite–wüstite (MW), is significantly lower than that previously reported for Hawaiian lavas (~FMQ). Similarly, rapidly quenched lavas from the ongoing Kilauea eruption and Loihi seamount, all have oxygen fugacities that are close to MW and on the low side of the range previously reported for Hawaiian lavas. From this we conclude that the initial oxygen fugacity of parental Hawaiian magmas is close to MW, not FMQ, and that previous estimates of the oxidation state of Hawaiian lavas may have been too high. This implies that the plume source of these magmas is also at or below MW, but not as reduced as the mantle source of mid-ocean ridge basalts. Additionally, Mauna Loa lavas appear to be slightly more reduced than Kilauea or Loihi lavas, perhaps indicating heterogeneous oxidation within the Hawaiian plume.

Introduction

The oxygen fugacity of basaltic magma is a fundamental intensive variable that controls the iron redox state ($Fe_2O_3/FeO+Fe_2O_3$) of the melt. It has a strong influence on the sequence and composition of minerals crystallizing from a cooling magma, and therefore on the composition of fractionated melts. More importantly, perhaps, the oxygen fugacity of basaltic magmas is thought to reflect the oxygen fugacity of their mantle source (e.g., Basaltic Volcanism Study Project 1981; Carmichael and Ghiorso 1986; Wood et al. 1990; Carmichael 1991) or at the very least to place an upper limit on that of the source (Ballhaus 1993; Ballhaus and Frost 1994). The oxidation state of the mantle has been the subject of considerable debate and controversy over the last 2 decades (e.g. Arculus 1985; O'Neil and Wall 1987; Haggerty 1990; Wood et al. 1990; Ballhaus 1993, 1995). In principle, it should range from reduced mantle in equilibrium with the metallic core to oxidized mantle capable of producing oxidized basaltic magmas. Oxygen geobarometers that use the mineral assemblages of mantle-derived peridotites have proved to be a fruitful source of information about the oxygen fugacity of the lithosphere and asthenosphere. This option, however, is not available for the source of Hawaiian magmas because the peridotite xenoliths entrained in the rejuvenated Hawaiian alkalic basalts are thought to represent fragments of the oceanic lithosphere and not the plume source of Hawaiian magmas (e.g., Frey and Roden 1987). Therefore, the oxidation states of the magmas themselves are probably the best available source of information

To date, most information on the oxidation states of Hawaiian magmas come from analyses of lavas erupted on Kilauea volcano. There is no comparable information for other Hawaiian volcanoes. At first glance it might appear that the oxidation state of Kilauea magmas has been well established as being within plus or minus one log unit of the fayalite-magnetite-quartz (FMQ) buffer. Early studies of Kilauea's lava lakes using direct in situ measurements with the ZrO_2 electrolytic cell technique, yielded oxygen fugacities slightly above FMQ over a range of temperatures (Fudali 1965; Sato and Wright 1966; Peck and Wright 1966). Similarly, studies using the ilmenite–magnetite geothermometer and oxygen geobarometer of Buddington and Lindsey (1964) report oxygen fugacities that are above

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FMQ, but below the nickel–nickel oxide (NNO) buffer (Wright and Weiblen 1968; Anderson and Wright 1972). More recently, using the Spencer and Lindsley (1981) modification of this technique, Helz and Thornber (1987) obtained an oxygen fugacity at NNO for magnetite–ilmenite pairs in cores from the Kilauea Iki lava lake. These results for Kilauea are within the range of oxygen fugacities compiled for oceanic (island and seafloor) basalts, but are slightly higher than oxygen fugacities compiled for continental basalts (Basaltic Volcanism Study Project 1981).

The oxide oxygen geobarometer is, however, restricted to lavas in which magnetite and ilmenite are in equilibrium, i.e., at temperatures typically below 1,080°C in Kilauea lavas (Helz and Thornber 1987), with the consequence that its use is confined to slowly cooled flows, lava lakes and evolved lavas (Helz and Thornber 1987). On the other hand, these results are broadly consistent with the analyses of volcanic gases (Gerlach 1980, 1993). Gerlach argues that the gases from Kilauea, which have oxygen fugacities midway between NNO and FMQ, reflect the oxygen fugacity of the associated lava over a temperature range from around 1,185°C to below the solidus at 980°C (Helz and Thornber 1987): in other words, well within the temperature range of many surface lava flows.

An alternative approach for estimating the oxidation state of basaltic magmas uses the experimental calibration of Fe_2O_3/FeO in the melt with temperature and oxygen fugacity (Sack et al. 1980; Kilinc et al. 1983; Kress and Carmichael 1991). Carmichael and Ghiorso (1986) applied this method to calculate oxygen fugacities from published analyses of Fe_2O_3 and FeO in 59 glassy basalts. Most of these came from Kilauea, and have a range in oxygen fugacity of around 2 log units. The average is slightly below FMQ, and about 0.5 log units more reduced than the earlier estimates. In this and subsequent papers, Carmichael and Ghiorso (1986) report the oxygen fugacity relative to the NNO buffer. This is because there is little change in $Fe_2O_3/(FeO + Fe_2O_3)$ in the melt if it is equilibrated at various temperatures with an external buffer such as NNO or FMQ. ΔNNO is defined as $\log_{10}$ fugacity O_2(sample)$-\log_{10}$ fugacity O_2 (NNO). The range in ΔNNO they obtained for Kilauea lavas is from -2.0 to 0.1 with an average of -1.08 (Fig.1). Because these subaerial Kilauea lavas are more reduced than undegassed submarine lavas from below 3,500 m on Kilauea's submarine east rift zone, Carmichael and Ghiorso (1986) speculate that the submarine lavas may best reflect the initial oxygen fugacity of Kilauea parent magmas prior to eruption, and that the subaerial lavas may have become reduced on eruption through sulfur degassing; that is, that the oxidation state of Kilauea's parental magmas is slightly above FMQ with a ΔNNO of around -0.5 to -0.6. Sulfur reduction of this kind was previously predicted by Anderson and Wright (1972) from zoning in iron–titanium oxides.

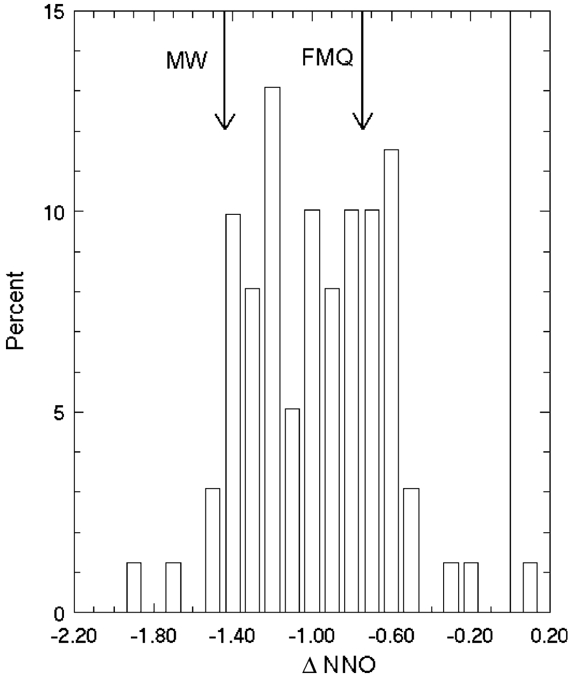

Fig. 1 *Histogram* taken from Carmichael and Ghiorso (1986) of ΔNNO values for subaerial Kilauea lavas. Also shown are the FMQ and MW oxygen buffers calculated at 1,200°C

In this paper, we present oxygen fugacities calculated from Fe_2O_3/FeO abundances in lavas erupted on Mauna Loa in 1984. We show that they are significantly lower than those reported for Kilauea, and argue that how, when and where a sample is taken is of critical importance in determining its oxidation state. We speculate further that the oxidation state of Hawaiian parental magmas may not be as high as is commonly perceived, or that there are real differences between different volcanoes, reflecting differences in the oxidation state within the Hawaiian mantle plume.

The 1984 Mauna Loa eruption

The following brief account of the 1984 Mauna Loa eruption is taken from Lockwood et al. (1987) and Rhodes (1988) and is summarized in Fig. 2. The eruption started on March 25th at 01:30 h in the summit caldera, Mokuaweoweo. Eruptive fissures rapidly propagated across the caldera and briefly extended into the upper southwest rift zone. At 03:57 h, activity migrated to the upper northeast rift zone, and further activity in the caldera ceased by 07:00 h. At 09:10 h, new eruptive fissures opened at a lower elevation on the northeast rift zone between 3,400 m and 3,500 m, in the vicinity of Dewey Cone. These remained active for the next 21 h and produced a short flow down the southeast flank of the volcano (Fig. 2). At 16:41 h on the same day, new vents opened up about 15 km down the northeast rift zone, near Puu Ulaula, between 2,770 m and 2,930 m. Other activity quickly waned, and

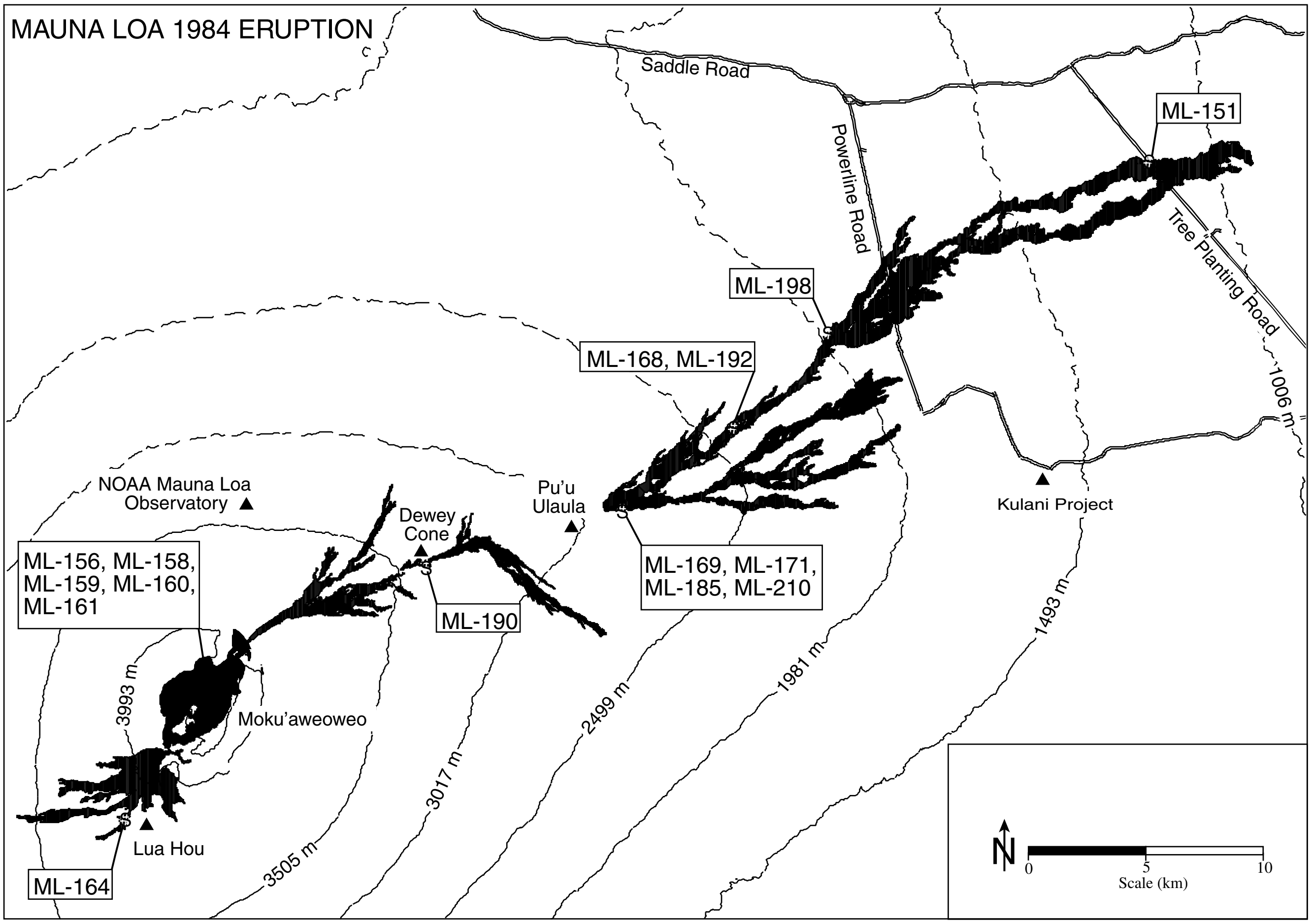

Fig. 2 Map of the 1984 Mauna Loa eruption showing sample localities

subsequent eruptions were restricted to these vents for the next 22 days. The eruption ceased on April 15th having produced about 220×10^6 m^3 lava, 90% of which was erupted from the lowermost vents.

The 1984 lavas are aphyric, with rare, scattered olivine phenocrysts. These olivines are probably xenocrysts because the forsterite content (Fo_{89}) is too high to be in equilibrium with the host lavas (~Fo_{81}). In a detailed study, Rhodes (1988) showed that the composition of these lavas was remarkably uniform throughout the entire 22 days of the eruption and along the 20-km vent system. Although the lava composition and temperature remained constant throughout the eruption, there was an increase in the proportions of microphenocrysts of plagioclase, clinopyroxene and olivine as the eruption progressed that correlated with a decline in the eruption rate (Lipman et al. 1985; Rhodes 1988). The fact that the proportions of these microphenocrysts increased from about 1% during the early stages of the eruption to around 30% on the last day, without any changes in bulk composition, emphasizes that there was no effective mechanism for melt-crystal fractionation throughout the eruption (Rhodes 1988). Therefore, bulk analyses provide reliable estimates of the magma composition.

We have selected a subset of 15 samples from this earlier study (Rhodes 1988) to investigate the oxidation state of these magmas. The samples included rapidly chilled spatter collected immediately after the eruption from vents in the caldera and upper southwest rift zone; water-quenched samples taken from active pahoehoe toes, close to the main vent at the 2,900-m level; and water-quenched lava scooped from the surface of active flows several kilometers away from the vents. Additionally, a solidified aa core, sampled after the eruption, was also analyzed. Sample locations are shown in Fig. 2.

Analytical methods

We have determined the oxygen fugacity of samples of the 1984 lavas using the experimentally determined relationship between $Fe_2O_3/(FeO + Fe_2O_3)$ in the melt and temperature and oxygen fugacity (Kilinc et al. 1983; Kress and Carmichael 1991). Temperatures are estimated from quenched whole rock compositions using the MgO in glass geothermometer of Montierth et al. (1995). This geothermometer is similar to that of Helz and Thornber (1987) for Kilauea lavas, but differs slightly from it in detail, and is more appropriate for Mauna Loa compositions. These calculated temperatures tend to be around 30°C higher than in situ measurements obtained with a chrome–alumel thermocouple. Ferrous iron is determined titrimetrically in duplicate on separate 150–200 mg aliquants of whole-rock powder, using the cold-acid digestion technique introduced by Wilson (Wilson 1955, 1960; Maxwell 1968). This method has the advantage that the samples are digested in a cold mixture of hydrofluoric and sulfuric acids in the presence of an excess of ammonium metavanadate, thereby, avoiding problems associated with the oxidation of the sample during digestion and subsequent analysis. The precision of the FeO measurements is around ±0.07 −0.11% (2σ). Replicate analyses of the basaltic NIST standard SRM-688 gave a mean FeO value of 7.57%, which compares with the certified value of 7.64%. Ferric iron is obtained by difference from total iron, obtained by X-ray fluorescence analysis (XRF) along with the other major elements. Trace elements and sulfur are also determined by XRF. The XRF techniques, precision and accuracy are the same as those described in Rhodes (1996) and Rhodes and Vollinger (2004). The precision for duplicate analyses of total iron as Fe_2O_3 of an in-house standard HSDP-1 is ±0.05% (2σ) with a mean value of 12.10%. This standard is from the Kilauea 1919 flow from which the USGS standard BHVO-1 was taken. Our value for BHVO-1 is 12.17% compared with 12.23% for the preferred value (Potts et al. 1992).

Because Fe_2O_3 is a relatively small number, derived from the difference between total iron as Fe_2O_3 and FeO, its errors will be controlled by the errors of the other two variables. The error on a variable that is derived from the sum or difference of two variables is given by the square root of the sum of the variances of the two variables (Taylor 1982). Substituting the estimates of precision for total Fe_2O_3 and FeO, discussed above, provides an estimate of the precision for Fe_2O_3 between ±0.08% and 0.11% (2σ) for duplicate analyses.

Since oxygen fugacity is obtained from Fe_2O_3/FeO (Kilinic et al. 1983; Kress and Carmichael 1991), the errors associated with this ratio will propagate into calculated oxygen fugacities.

The error of the ratio (Fe_2O_3/FeO) is obtained from the square root of the sum of the squares of the errors for Fe_2O_3 and FeO (Taylor 1982). Using the errors estimated above for Fe_2O_3 and FeO gives an error for Fe_2O_3/FeO of ±0.0115 (2σ) for duplicate measurements. This translates into an error in the calculated oxygen fugacity (log fO_2) of ±0.18 (2σ). The data are given in Table 1.

Results

The four molten samples, quenched in water, from close to the main vents at the 2,900 m level (ML-169, ML-171, ML-185, and ML-210) were collected throughout the eruption between March 29th and April 15th. ML-210 was the "last gasp" ooze-out on the very last day of the eruption. All have oxygen fugacities below or at the MW

Table 1 Composition and oxygen fugacity of 1984 Mauna Loa lavas

Sample	ML156	ML158	ML159	ML160	ML161	ML164	ML169	ML171	ML185	ML210	ML190	ML168	ML192	ML198	ML151
Mo/Da	3/25	3/25	3/25	3/25	3/25	3/25	4/1	3/29	4/4	4/15	3/25	3/31	3/26	4/08	3/29
Type	Spatter	Spatter	Spatter	Spatter	Spatter	Spatter	Q. vent	Q. Vent	Q. vent	Q. vent	Q. flow	Q. flow	Q. flow	Q. flow	Aa
Elevation (m)	3,990	3,983	3,981	3,984	3,975	3,889	2,900	2,900	2,900	2,900	3,490	1,950	1,950	2,427	1,150
SiO_2	51.98	51.97	52.13	52.02	52.02	52.41	52.01	52.36	52.36	52.09	51.90	52.47	51.91	51.79	52.23
TiO_2	2.14	2.09	2.14	2.11	2.09	2.20	2.13	2.11	2.10	2.08	2.10	2.10	2.09	2.07	2.12
Al_2O_3	13.81	13.85	13.92	13.81	13.77	13.74	13.72	13.86	13.77	13.80	13.85	13.84	13.76	13.73	13.89
Fe_2O_3	0.97	1.08	1.36	1.02	0.84	1.12	0.81	1.03	0.74	1.00	1.50	1.10	2.59	3.40	2.63
FeO	9.92	9.85	9.68	9.93	10.08	10.02	10.13	10.04	10.20	10.00	9.49	9.93	8.48	7.81	8.55
MnO	0.18	0.20	0.17	0.18	0.19	0.17	0.19	0.17	0.19	0.19	0.19	0.19	0.20	0.20	0.15
MgO	6.71	6.84	6.86	6.75	6.74	6.50	6.82	6.84	6.78	6.82	6.73	6.96	6.71	6.78	6.75
CaO	10.62	10.56	10.72	10.66	10.58	10.53	10.58	10.70	10.61	10.59	10.61	10.68	10.57	10.55	10.70
Na_2O	2.69	2.62	2.59	2.72	2.56	2.50	2.37	2.59	2.51	2.58	2.71	2.45	2.83	2.60	2.46
K_2O	0.39	0.39	0.38	0.39	0.40	0.44	0.38	0.40	0.39	0.39	0.38	0.38	0.40	0.39	0.39
P_2O_5	0.25	0.25	0.24	0.26	0.26	0.28	0.23	0.26	0.26	0.25	0.23	0.24	0.24	0.25	0.24
Total	99.66	99.70	100.19	99.85	99.85	99.91	99.37	100.36	99.91	99.79	99.69	100.34	99.78	99.57	100.11
S ppm	235	1,000	525	310	180	105	65	60	60	70	90	55	25	145	25
$T_{measured}$							1,129	1,136	1,145			1,137	1,131		
$T_{calculated}$	1,166	1,169	1,170	1,167	1,167	1,162	1,169	1,169	1,168	1,169	1,167	1,172	1,166	1,168	1,167
Log fO_2	−9.86	−9.58	−9.08	−9.75	−10.14	−9.62	−10.17	−9.72	−10.40	−9.76	−8.90	−9.51	−7.62	−6.85	−7.54
ΔNNO	−1.90	−1.65	−1.16	−1.80	−2.19	−1.61	−2.24	−1.79	−2.46	−1.83	−0.94	−1.61	0.35	1.09	0.42

(magnetite–wüstite) buffer with ΔNNO between −1.8 and −2.5 (Table 1; Fig. 3). We found no significant systematic change in the oxygen fugacity of these vent samples throughout the 22-day eruption. The spatter samples (ML-156, ML-158, ML-159, ML-161, and ML-164) were erupted within the summit caldera and the upper southwest rift zone during the first few hours of the eruption, but were collected several days later. All but one of these have low oxygen fugacities, similar to the quenched vent samples, again plotting at or below MW with ΔNNO between −1.6 and −1.9 (Table 1; Fig. 3). One spatter sample from within the caldera (ML-159) is slightly more oxidized than the others, plotting between MW and FMQ (Fig. 3) with a ΔNNO of −1.2.

In contrast with the rapidly quenched (both natural and artificial) vent samples, water-quenched lava flow samples show highly variable oxygen fugacities from values at MW to values well above NNO, with ΔNNO ranging from −1.6 to 1.09. The flow sample with the lowest oxygen fugacity (ML-168), on the MW buffer (ΔNNO at −1.61), was taken on the seventh day of the eruption, and was scooped from the flow through a skylight of a lava tube at 1,950-m elevation, just above the Powerline road (Fig. 2), about 11-km below the main vents. The next least-oxidized flow sample (ML-190) was scooped and quenched from the surface of a pahoehoe flow close to the vents at around 3,490-m elevation. The oxygen fugacity was between FMQ and MW (Fig. 3), with ΔNNO at −0.94. The two most-oxidized flow samples (ML-198 and ML-192), with oxygen fugacities above NNO (ΔNNO of 1.09 and 0.35, respectively), were scooped and water-quenched from the surface of the main aa channel at 2,427 and 1,950-m elevations, about 5 and 10-km below the main vent, respectively. Note that these values are comparable with the value of −7.5 (ΔNNO at 0.42) obtained for the solidified core of the aa flow (ML-151) taken at the Tree Planting road at 1,150-m elevation (Figs. 2 and 3).

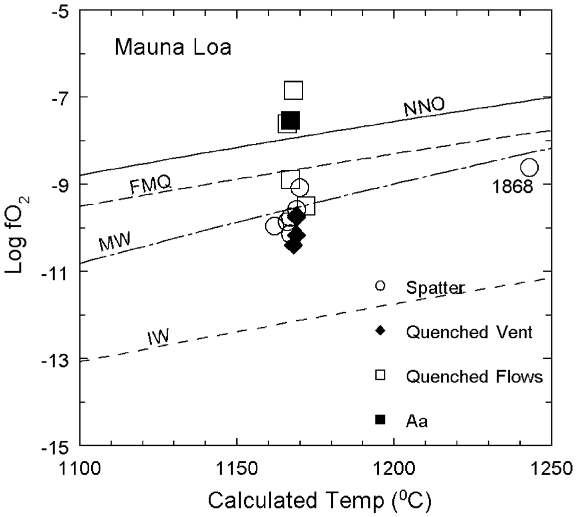

Fig. 3 Calculated oxygen fugacity versus temperature for 1984 Mauna Loa lavas. Temperatures are calculated using the MgO in glass geothermometer for Mauna Loa lavas of Montierth et al. (1995). Spatter samples are shown as *open circles*; quenched near-vent samples as *solid diamonds*; quenched flow samples as *open squares* and a solidified aa sample as a *filled square*. Shown for reference are the oxygen buffer curves for nickel–nickel oxide (*NNO*), fayalite–magnetite–quartz (*FMQ*), magnetite–wüstite (*MW*) and iron–wüstite (*IW*). Also shown is glassy matrix from 1868 picritic spatter (Rhodes 1995)

Also plotted in Fig. 3 is data for hand-picked glassy matrix of spatter collected from the picritic 1868 eruption (Rhodes 1995). Although at a higher temperature, it also has an oxygen fugacity below MW (ΔNNO at −1.54), consistent with the results for spatter and quenched vent samples from the 1984 eruption.

Discussion

Sampling effects

It is clear that the oxidation state of these samples depends very critically on where, when and how the samples were taken. Rapidly chilled samples, collected at, or close to, a vent, whether chilled in air, as in the case of spatter, or water-quenched pahoehoe toes, are the least oxidized. They have values below, or close to, MW, with ΔNNO typically between −1.6 and −2.5 (Fig. 3). Thus, they lie on the low side of the range found by Carmichael and Ghiorso (1986) for Kilauea lavas, and extend to even lower values (Fig. 1). Conversely, and despite rapid quenching in water, lava that has traveled any significant distance from the vents and is exposed to air has become much more oxidized, with ΔNNO ranging from −0.9 to 1.1. The low ΔNNO value, similar to that of spatter and quenched vent samples, for sample ML-168, which was scooped from a skylight in a lava tube, suggests that oxidation is much less effective in lava tubes than in open channels.

We elected to see if these obvious effects of sampling on the oxidation state of lavas are evident in other Hawaiian data sets. Neal et al. (1988) reported "wet chemical" analyses of lavas erupted during the first 20 episodes (1983–1984) of the ongoing Puu Oo eruption of Kilauea. They did not, however, calculate or comment on the oxidation state of the lavas. For the most part, the lavas are glassy with few phenocrysts, so bulk analyses are appropriate representations of the melt composition. We have calculated oxygen fugacities from Fe_2O_3 and FeO abundances reported in this data and using temperatures estimated from the Kilauea MgO in glass geothermometer of Helz and Thornber (1987). Samples of lava and spatter that were collected in the molten state and rapidly quenched in water typically have oxygen fugacities between MW and FMQ (Fig. 4), with ΔNNO ranging from −2.9 to 0.1. Figure 5 shows that, although overlapping the range for Kilauea lavas given by Carmichael and Ghiorso (1986), the vast majority are on the low side. However, lavas that were sampled after cooling, even though they are also glassy,

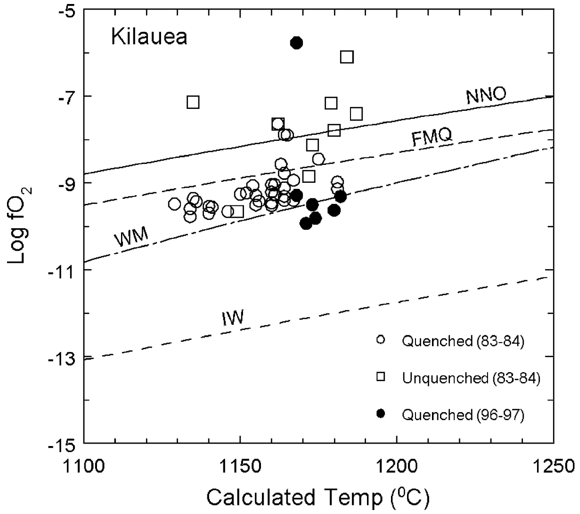

Fig. 4 Calculated oxygen fugacity versus temperature for the ongoing (1983–present) Kilauea eruption. Data are taken from Neal et al. (1988) and Roeder et al. (2003) and temperatures are calculated using the Helz and Thornber (1987) MgO in glass geothermometer for Kilauea lavas. Quenched samples are shown as *circles* and unquenched samples as *open squares*. Shown for reference are the oxygen buffer curves for nickel–nickel oxide (*NNO*), fayalite–magnetite–quartz (*FMQ*), magnetite–wüstite (*MW*) and iron–wüstite (*IW*)

have higher calculated oxygen fugacities (Fig. 4), ranging from values that are similar to the quenched lavas (ΔNNO ~ −1.5) to oxidized values slightly above NNO (ΔNNO ~0.1). That is, the slowly cooled lavas have values that are comparable to the range shown by Carmichael and Ghiorso (1986) and previously published Kilauea values (Fudali 1965; Sato and Wright 1966; Peck and Wright 1966; Wright and Weiblen 1968; Anderson and Wright 1972; Helz and Thornber 1987). Additionally, Roeder et al. (2003) report oxygen fugacities for quenched lavas sampled from the ongoing Kilauea eruption between 1996 and 1997, using both Fe_2O_3 and FeO abundances in the lavas, and also using a new oxygen geobarometer based on the distribution of Cr between melt and spinel (Poustovetov and Roeder 2001). Both methods are in agreement and indicate that these lavas are also at or below MW (Fig. 4), with ΔNNO values between about 1.4 and 2.0 log units below NNO: again, very much on the low side of the range given by Carmichael and Ghiorso (1986).

From this, we conclude that even short-term exposure to air, or the potential for hydrogen loss due to dissociation of H_2O (Christie et al. 1986), can result in significant over-estimation of the magmatic oxygen fugacity. These results, although compelling, should come as no surprise. Washington (1923) noted that glassy lavas have lower Fe_2O_3 than more crystalline lavas, even within the same flow. Similarly, Moore and Ault (1965) showed that the more rapidly cooled portions of the same flow had lower Fe_2O_3 than more slowly cooled portions. More recently, Christie et al. (1986) made the important discovery that the rapidly chilled glassy rims of mid-ocean ridge pillow basalts contain less Fe_2O_3, and therefore were more reduced than the pillow interiors. They concluded that the glassy rims provide a better estimate of magmatic conditions, indicating much lower oxygen fugacities (about 1–2 log units below FMQ and with ΔNNO about −1.5 to −3.0) than measurements on pillow interiors. They speculated that the reason for the discrepancy between the pillow interiors and the glassy margins was dissociation of H_2O and the loss of hydrogen from the slower-cooled pillow interior. The important implications here are that MORB magmas are more reduced than was previously thought, with the corollary that the mantle source of MORB is also reduced. This inference has been substantiated by the determination of comparable oxygen fugacities, using the olivine–orthopyroxene–spinel oxygen geobarometer, in oceanic peridotite, thought to be the residues remaining after melting to produce MORB (e.g., Wood et al. 1990).

The oxidation state of Hawaiian magmas

The prevailing consensus on the oxidation state of Hawaiian magmas is that they are close to FMQ, possibly slightly higher if sulfur degassing has resulted in reduction of the magma. Clearly, our results for the 1984 Mauna Loa eruption are at variance this opinion. Rapidly chilled samples from vent areas have oxygen fugacities below, or at, MW (ΔNNO about −1.6 to −2.5). This is up to 2.5 log units below NNO and 1.8 log units below FMQ, and below the previous range of values ascribed to Hawaiian lavas (Carmichael and Ghiorso 1986), but not as reduced as values reported by Christie et al. (1986) for MORB (ΔNNO about −1.5 to −3.0).

It has been suggested that oxygen fugacities are lowered by sulfur de-gassing and that parental Hawaiian magmas have oxygen fugacities between FMQ and NNO (Carmichael and Ghiorso 1986). This argument has also been used by Roeder et al. (2003, 2004) to reconcile oxygen fugacities below MW obtained for the ongoing Kilauea eruption (see Fig. 4) with higher estimates, between FMQ and NNO, based on gas data for the same eruption (Gerlach1993, 2004).

This cannot be the explanation for the low oxygen fugacities obtained for the 1984 Mauna Loa lavas. The sulfur content of these samples is quite variable (Table 1). Spatter samples erupted within the caldera on the first day of the eruption show the highest values, ranging from 180 ppm to 1,000 ppm. On the other hand, samples erupted from lower vents contain much less sulfur (25–145 ppm), consistent with the observation that these samples are extensively de-gassed (Lipman et al. 1985). There is no positive correlation between sulfur content and oxidation state, and in fact the most oxidized samples tend to have the lowest sulfur contents. This is contrary to what one would expect if sulfur de-gassing was the cause of the differences in oxidation state.

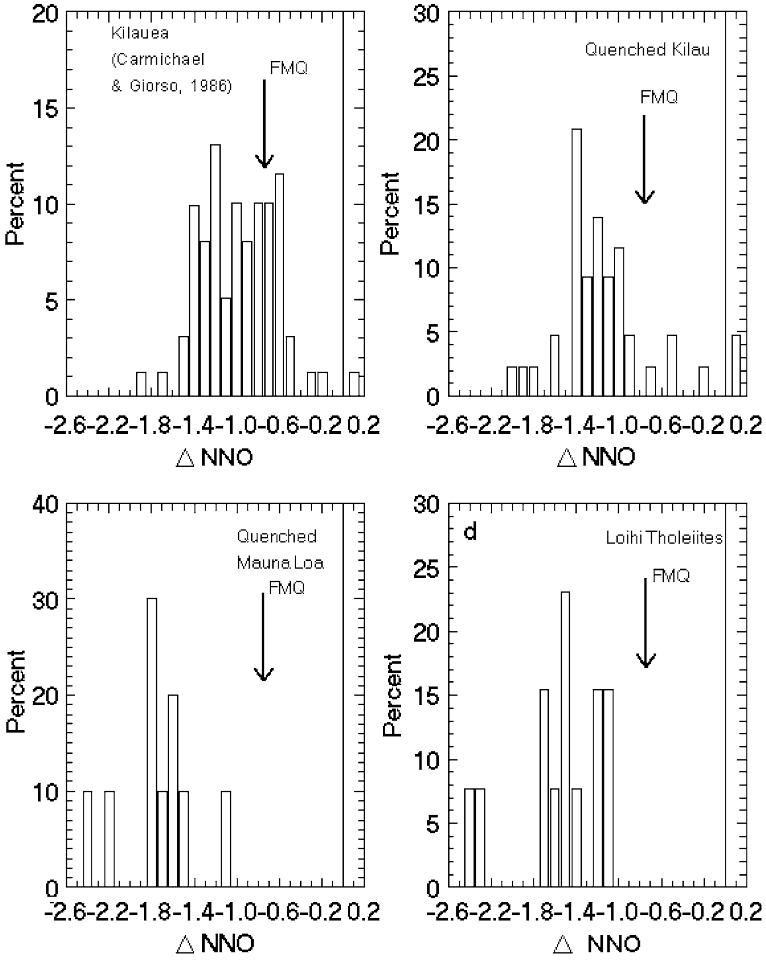

Fig. 5 *Histograms* comparing the range and distribution of ΔNNO values for: **a** unquenched Kilauea lavas from Carmichael and Ghiorso (1986); **b** quenched lavas from the ongoing Kilauea eruption from Neal et al. (1988) and Roeder et al. (2003); **c** quenched lavas from Mauna Loa (this study), and **d** basaltic submarine tholeiitic and transitional basalt pillow margins from Loihi seamount from Byers et al. (1985) and Wallace and Carmichael (1992). The *arrows* show the approximate position of the fayalite–magnetite–quartz (*FMQ*) buffer

The fact that the much hotter 1868 picritic eruption was similarly reduced (Fig. 3) suggests that these values reflect the initial oxidation state of Mauna Loa magmas: a finding that is in accord with the prediction, based on Ni partitioning between olivine and melt, that the oxidation state of Mauna Loa magmas is close to MW (Morse et al. 1991). These results imply that either the previous estimates of the oxidation state of Hawaiian magmas are too high, or there are real differences in the oxidation state of magmas from individual Hawaiian volcanoes, with Mauna Loa magmas being more reduced than those from Kilauea.

Support for both interpretations comes from the ongoing (1983–present) Puu Oo eruption of Kilauea (Neal et al. 1988; Roeder et al. 2003) and from submarine pillow lavas from Loihi seamount (Byers et al.1985; Wallace and Carmichael 1992). We have shown earlier that, as for the 1984 Mauna Loa eruption, rapidly quenched samples from close to the vents of the ongoing Kilauea eruption also have low oxygen fugacities, with ΔNNO mostly between −0.9 and −2.0, and on the low side of the range for Hawaiian lavas (Figs. 4 and 5). The values for Mauna Loa are on the whole, lower than those for Kilauea, (Fig. 5) supporting the intriguing possibility that magmas from different Hawaiian volcanoes may have different oxidation states, just as they differ significantly in major and trace elements and isotopic ratios (e.g., Powers 1955; Wright 1971; Staudigel et al. 1984; Rhodes et al. 1989; Frey and Rhodes 1993; Lassiter and Hauri 1998). Current opinions on the nature of the Hawaiian plume, based largely on isotopic data, suggest that it is a heterogeneous mix of primitive mantle, recycled oceanic crust and lithosphere and entrained lower mantle (e.g., Frey and Rhodes 1993; Hauri et al. 1994; Kurz et al. 1995; Lassiter and Hauri 1998). Given this heterogeneity, it seems reasonable to infer that basaltic magmas derived from different parts of the plume may be in different oxidation states.

Byers et al. (1985) reported data, including Fe_2O_3 and FeO measurements, on the glassy margins of tholeiitic and alkalic pillow basalts from Loihi Seamount. Although they did not calculate oxygen fugacities, the Fe_2O_3/FeO in these lavas indicate that oxygen fugacities range over 2 log units from FMQ to below MW. Alkalic lavas tend to be the most oxidized, with tholeiitic and transitional lavas clustering at MW with ΔNNO values ranging between −1.3 and −2.4. Again, these are on the low side of the range reported by Carmichael and Ghiorso (1986) for Kilauea but compare closely with the range found for Mauna Loa lavas (Fig. 5). Data reported subsequently for Loihi by Wallace and Carmichael (1992) are consistent with these values. These submarine lavas, collected at depths of around 1,000 m, are not degassed, having sulfur abundances (0.08–0.24%) that are relatively high (Byers et al. 1985; Wallace and Carmichael 1992). This indicates that the reduced nature of these lavas is a fundamental characteristic of the magma and not a consequence of sulfur degassing as was proposed by Carmichael and Ghiorso (1986) for subaerial Kilauea lavas.

Conclusions

When, where and how a basaltic sample collected is critically important in determining its oxidation state. Rapidly cooled samples, either water-quenched or spatter, taken in close proximity to vents are less oxidized than quenched samples that have traveled some distance from the vents, or slowly cooled lavas sampled after an eruption. It appears that lava traveling in lava tubes may be less prone to oxidation than lava flowing in open channels.

Rapidly quenched samples from Mauna Loa have oxygen fugacities that are close to, or below, MW rather than FMQ, and are below, or overlap on the low side of the range previously reported for Hawaiian lavas (mostly Kilauea). Similarly, rapidly quenched lavas from the ongoing Kilauea eruption and Loihi seamount, all have oxygen fugacities that are close to MW and on the low side of the range previously reported for Hawaiian lavas. From this, we conclude that the initial oxygen fugacity of parental Hawaiian magmas is close to MW not FMQ, and that previous estimates of the oxidation state of Hawaiian lavas might have been too high. This implies that the plume source of these magmas is also at or below MW, but not as reduced as the mantle source of mid-ocean ridge basalts. In addition, since Mauna Loa lavas appear to be slightly more reduced than Kilauea or Loihi lavas, this may indicate heterogeneous oxidation within the Hawaiian plume.

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