

Temperatures and H₂O contents of low-MgO high-alumina basalts

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Abstract. Experimental evidence is used to estimate H₂O contents in low-MgO high-alumina basalts (HABs) (< 6 wt.% MgO) and basaltic andesites (BAs) (< 5 wt.% MgO) that occur worldwide in magmatic arcs. Whole-rock compositions of low-MgO HABs and BAs, phenocryst assemblages, and mineral chemistry match the compositions of liquids, phase assemblages, and mineral-compositions produced in H₂O-saturated melting experiments on HABs at moderate pressure (1–2 kb). Low-MgO HABs and BAs therefore could have existed as H₂O-rich multiply-saturated liquids within the crust. Results are presented for melting experiments on two HABs and an andesite at 1 kb pressure, H₂O-saturated, with *f*O₂ at the NNO buffer. These data and other experimental results on HABs are used to develop a method to estimate the temperature and H₂O content of HAB or BA liquids saturated with olivine, plagioclase, and either high-Ca pyroxene or hornblende. Estimated H₂O contents of HAB liquids are variable and range from < 1 to > 8 wt.%. High-MgO HABs (> 8 wt. % MgO) could have H₂O contents reaching no more than 1–2 wt.%. The more common low-MgO HABs could have existed as liquids within the crust with H₂O contents of 4 wt.% or higher at temperatures < 1100 °C. Magmas with these high H₂O contents will saturate with and exsolve aqueous fluid upon approaching the surface. They cannot erupt as liquids and must grow crystals at shallow depths, thus accounting for the abundant phenocrysts in low-MgO HABs and BAs.

Introduction

Convergent margin mafic magmatism is characterized on a global scale by the eruption of high-alumina basalts (HABs) and basaltic andesites (BAs), most of which have

compositions too evolved to be immediately derived from mantle peridotite. These low-MgO HABs and BAs are present in most arcs and are the dominant volcanic product in some arcs such as the Aleutians (Marsh 1982; Kay and Kay 1992) and Central America (Carr and Rose 1987). The ubiquity and regional abundance as well as the relatively uniform compositions of low-MgO HABs and BAs suggests that these magmas form under similar conditions and by similar processes in all arcs and that discovering these conditions will reveal key aspects of arc magma genesis. Two end-member petrogenetic models have been developed to explain low-MgO HABs. Marsh (1982) and coworkers have held that low-MgO HABs originate by large degree melting of subducted, metamorphosed, and dehydrated ocean crust. An alternative model, presented by S. Kay and coworkers (1982), argues that common low-MgO HABs form by crustal-level crystallization differentiation of mantle-derived magnesian basalts that erupt less frequently than their high-alumina daughters. While some geologic evidence favors the differentiation model (Kay and Kay 1992), experimental studies on anhydrous HABs have failed to produce the requisite fractionating minerals and HAB liquids at crustal or upper mantle pressures (Baker and Eggler 1983; Johnston 1986).

An allied subject is the role of H₂O in generating arc magmas and affecting their subsequent differentiation. Coats (1962) first proposed that subducted ocean crust and sediments give up their H₂O either as a fluid or hydrous partial melt that enters and influences the differentiation of mantle-derived basaltic magmas. This general model has been widely embraced, with various small modifications, but there are few quantitative estimates of the pre-eruptive H₂O contents of mafic arc magmas upon which one can build more precise petrogenetic models. The melting mechanisms and amounts of H₂O in primary arc magmas are unknown. By analogy with MORBs and ocean island basalts, arc basalts are generally thought to have low H₂O contents.

In the present study we combine these issues by using new experimental results presented herein and in a companion manuscript (Sisson and Grove 1992, *this issue*) to

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Table 1. High-alumina basalts and basaltic andesites with low MgO contents

	Rocks						Groundmass and residual liquids			Glass inclusions		
	1	2	3	4	5	6	7	8	9	10	11	12
SiO ₂	52.1	50.6	51.4	52.5	51.3	53.7	53.0	51.3	53.3	51.9	50.1	53.0
Al ₂ O ₃	19.7	20.9	19.8	18.4	19.4	18.8	19.0	19.2	17.8	19.5	20.6	18.9
FeO*	8.75	9.26	9.47	10.6	8.81	8.52	9.18	10.1	10.5	10.1	8.98	6.68
MgO	4.46	3.69	5.10	3.9	4.38	4.36	3.44	4.46	4.21	4.8	3.70	5.72
CaO	10.0	10.3	9.18	8.2	8.98	7.84	9.48	9.58	9.04	9.4	11.3	11.0
Na ₂ O	2.80	3.27	3.47	3.8	4.29	3.99	3.92	3.23	3.13	2.72	3.53	3.31
K ₂ O	0.77	0.71	0.77	1.14	1.01	0.71	0.78	0.99	0.83	0.65	0.48	0.46
TiO ₂	0.96	0.91	0.90	1.30	1.29	1.61	1.18	0.86	0.89	0.90	1.08	0.85
MnO	0.17	0.18			0.17		0.14	0.23	0.25		0.24	
P ₂ O ₅	0.30	0.16		0.25	0.38	0.29						
Total: All analyses normalized to total 100%, volatile-free, with all Fe as FeO.												
Mg#	0.48	0.42	0.49	0.40	0.47	0.48	0.40	0.44	0.42	0.46	0.42	0.60
CaO/Al ₂ O ₃	0.51	0.49	0.46	0.45	0.46	0.42	0.50	0.50	0.51	0.48	0.55	0.58

1. Average Cold Bay HAB, Aleutians (n = 7, Brophy 1986). 2. Average Atka HAB, Aleutians (n = 18, Myers et al. 1986). 3. Average Fuego, Guatemala 1974 eruptive (Rose et al. 1978). 4. Hornblende HAB, Ayarza, Guatemala (Peterson and Rose 1985). 5. Aphyric hornblende HAB sill, Onion Valley, Sierra Nevada batholith, CA (Sisson 1991). 6. Aphyric high-alumina BA, Sidara basin, Japan (Kuno 1960). 7. Average groundmass, Fuego, Guatemala 1974 eruption (Rose et al. 1978). 8. Average residual liquid with SiO₂ < 52% and Al₂O₃ > 17% in hornblende-bearing cumulate xenoliths, Lesser Antilles (n = 4, Arculus and Wills 1980). 9. Average residual liquid with SiO₂ 52-55%, Al₂O₃ > 17% in hornblende-bearing cumulate xenoliths, Lesser Antilles (n = 3, Arculus and Wills 1980). 10. Average low-K₂O glass inclusion in olivine, Fuego, Guatemala 1974 eruption (n = 7, Harris and Anderson 1984). 11. Average glass inclusion with SiO₂ < 54%, Soufriere, St. Vincent 1979 eruption (Devine and Sigurdsson 1983). 12. Average glass inclusion with SiO₂ ≤ 55%, Al₂O₃ > 17%, Mt. Shasta, California (n = 19, Anderson 1973, 1974, 1979, 1982)

Table 1 (continued)

Representative hydrous 2-kb experimental liquids saturated with plag - oliv - high-Ca pyx or hornblende

	1	2	3	4	5
SiO ₂	51.5	51.8	52.5	52.1	53.9
Al ₂ O ₃	19.2	19.4	19.2	19.3	18.5
FeO*	8.70	8.62	8.04	8.35	9.61
MgO	4.98	4.56	4.99	4.14	3.76
CaO	10.0	9.59	9.64	8.77	9.30
Na ₂ O	3.72	3.96	4.15	4.49	2.84
K ₂ O	0.42	0.45	0.21	0.99	0.11
TiO ₂	1.19	1.28	0.98	1.27	1.65
MnO	0.19	0.17	0.20	0.15	0.19
P ₂ O ₅	0.14	0.18	0.14	0.42	0.21
Total: Analyses normalized to 100%, volatile-free, with all Fe as FeO					
Mg#	0.51	0.49	0.53	0.47	0.41
CaO/Al ₂ O ₃	0.52	0.49	0.50	0.45	0.50

1. 1012 °C Ol-Cpx-Pl-H₂O. 2. 1000 °C Ol-Cpx-Pl-H₂O. 3. 1000 °C Ol-Cpx-Pl-Mt-H₂O. 4. 970 °C Ol-Hbl-Pl-H₂O. 5. 975 °C Ol-Cpx-Pl-Vapor (PH₂O ~ 0.7 P total, Spulber and Rutherford 1983). 1-4 from Sisson and Grove (1992)

explore the possibility that low-MgO HABs and BAs were H₂O-rich multiply-saturated liquids at crustal pressures. We find that they owe their major element compositions to simple mineral-melt phase equilibrium constraints at moderate pressure as has been found for most MORBs (Walker et al. 1979) and rhyolites (Tuttle and Bowen 1958), the other major magma types erupted on Earth. We argue that low-MgO HABs and BAs are not primary

melts of any anhydrous source nor are they differentiates of nearly anhydrous parent magmas. Instead, they likely form by differentiation of parent basalts with H₂O contents on the order of 2-4 wt. %.

Background

Kuno (1960) noted that basalts with high alumina contents are abundant along the Pacific rim in what are now recognized as magmatic arcs located above subduction zones. He discriminated between tholeiitic, alkali olivine, and high-alumina basalts on the basis of the petrographic and chemical characteristics of aphyric rocks. By Kuno's definition, HAB contained groundmass olivine with little or no reaction rim of low-calcium pyroxene. High-alumina basalt also contained more than 17 wt. % Al₂O₃ and could contain small amounts of either olivine or quartz in the norm (in addition to plagioclase, augite, and hypersthene). Kuno (1960) presented analyses of rocks with silica contents as high as 55 wt. % as representatives of the HAB magma series; these rocks would now be classified as basaltic andesites (Peccerillo and Taylor 1976). Kuno further observed that HABs are absent from regions that are now recognized as extensional or intraplate environments, even if plagioclase porphyritic rocks are considered.

Subsequent research has confirmed most of Kuno's (1960) observations on HABs. Most workers now use "high-alumina basalt" to refer to any volcanic rock with SiO₂ ≤ 52 wt. % (some use 54 %), Al₂O₃ > 17 wt. %, and an absence of significant normative nepheline. This definition encompasses a very broad range of rock compositions. Very many HABs and BAs have low MgO contents (< 6 wt. % and < 5 wt. % respectively) and low Mg numbers [Mg/(Mg + Fe) ~ 0.4-0.5], including some aphyric rocks (Kuno 1950, 1960; Marsh 1982; Carr et al. 1982; Brophy 1986; Myers et al. 1986). Typical low-MgO HABs and BAs also have alumina contents in the range 18.5-20.5 wt. % (Table 1), distinctly higher than Kuno's lower limit. Magnesian HABs are not unknown, however, and have compositions similar in many respects to magnesian mid-ocean ridge basalt glasses (Perfit et al. 1980).

Petrogenetic models

Models for the origin of HAB magmas fall into three general categories: (1) direct partial melts of either mantle or subducted slab (or some combination), (2) derivative liquids produced by fractional crystallization of other primary basalt magma, and (3) derivative liquids that have experienced preferential accumulation of plagioclase. Magnesian HABs have been proposed to be direct partial melts of the mantle wedge above a subducting plate. This model is supported by the experimental production of magnesian HAB liquid in equilibrium with a spinel-or plagioclase-lherzolite mineral assemblage under anhydrous conditions close to 10 kb (Fujii and Scarfe 1985; Takahashi 1986; Falloon and Green 1987; Bartels et al. 1991).

It has also been proposed that low-MgO HABs and BAs may be primary. According to this model, low-MgO HABs are created by dry melting of subducted oceanic crust that has transformed to eclogite (Marsh 1976, 1982). Trace element abundances require that most garnet is consumed during melting (Brophy and Marsh 1986). This constraint is difficult to reconcile with the observation that low and moderate-MgO HAB liquids have garnet as a liquidus mineral at appropriate pressures (Johnston 1986) although diapiric ascent of the entire source region could circumvent this objection (Brophy and Marsh 1986). Other arguments against this model are summarized by Crawford et al. (1987). In addition, most thermal models of the subducted slab suggest that temperatures generally are too low for dry melting of eclogite to occur (Anderson et al. 1978; Davies and Stevenson 1992).

A second model for the origin of low-MgO HABs is by fractional crystallization from a more primitive mantle-derived magma. It has proven difficult to reproduce the more MgO-poor HABs and BAs from MgO-rich HAB liquids by experimental crystallization under dry conditions (Gust and Perfit 1987; Bartels et al. 1991). The experimental mantle-saturated high-MgO HAB liquids are close to transitional and crystallization at elevated pressure drives residual liquids to nepheline normative compositions (Bartels et al. 1991). The resulting liquids are unlike common low-MgO HAB and BA. At low pressures, dry magnesian HAB crystallizes plagioclase usually accompanied by olivine and yields tholeiitic derivative liquids with low- Al_2O_3 , again unlike low-MgO HABs and BAs (Grove et al. 1982; Bartels et al. 1991). The difficulty of producing low-MgO HAB by crystallization of primitive aluminous parents has led to a third model: low-MgO HABs form by selective accumulation of plagioclase phenocrysts (Crawford et al. 1987). A different fractionation model is that low-MgO HABs are derivative liquids from the crystallization of olivine and high-Ca pyroxene from magnesian basalts (not high-alumina) found infrequently in some arcs (Kay et al. 1982; Nye and Reid 1986; Ramsay et al. 1984; Kay and Kay 1992). Johnston and Draper (1992) have recently shown that one of these magnesian but not high-alumina basalts could be a primary peridotite melt near 12 kb pressure. The fractionation model has merit as it accounts for the continuous variations in major and some trace elements observed in rock suites (Gust and Perfit 1987; Brophy 1986). Experimental studies have failed, however, to produce olivine on the liquidus of typical HABs with low (Baker and Eggler 1983, 1987) or moderate MgO contents (Johnston 1986) under what have been taken as plausible H_2O contents (e.g., anhydrous or nearly anhydrous), in apparent conflict with this model. In summary, none of the models based on anhydrous phase equilibria have been successful in producing the combined features of $\text{MgO} < 6$ wt.%, and $\text{Al}_2\text{O}_3 \sim 19$ wt. % in a hypersthene-normative basaltic magma that characterize the abundant low-MgO HABs.

H₂O in high-alumina basalt magmas

Most workers in arc petrology ascribe an important role to volatile components in the generation of arc magmas. The most plausible models for generation of arc magmas involve release of H_2O from the subducted slab which rises into the overlying hotter mantle and initiates melting either directly or through subsequent melting of amphibole (McBirney 1969; Tatsumi et al. 1983). The question is,

how much H_2O is in these melts? We summarize next geologic evidence consistent with high H_2O contents in HABs and BAs.

Yoder (1969) concluded that a highly aluminous magma containing highly calcic plagioclase is indicative of high magmatic H_2O contents. The presence of very calcic plagioclase is a characteristic of many mafic arc lavas, in the Aleutians up to An_{96} (Byers 1961; Brophy 1986; Singer et al. 1992; Kay and Kay 1992), in Guatemala up to An_{97} (Anderson 1984), and in Japan up to An_{95} , (Kuno 1950). Marsh et al. (1990, their Fig. 9) show, based on thermodynamic models, that H_2O contents of 5–6 wt.% would be required for observed calcic plagioclase to have grown from liquids with the composition of typical Aleutian HAB or andesite (excessive in the opinion of those authors). The presence of early-formed hornblende is unequivocal evidence for high melt H_2O contents. Baker and Eggler (1983) show that more than 4.5 wt. % H_2O is necessary to stabilize amphibole near or on the liquidus of low-MgO HAB melt at 2 kb. Hornblende-bearing cumulate inclusions from the Lesser Antilles (Arculus and Wills 1980) also composed of olivine, high-Ca pyroxene and calcic plagioclase (An_{90} - An_{100}) have trapped low-MgO HAB as intercumulus glass and quenched matrix (Table 1) and are compelling evidence for the existence of hydrous HAB liquids in the crust. Hornblende has also been erupted as rare phenocrysts coexisting with calcic plagioclase, salitic pyroxene with and without olivine in HABs and BAs in Central America (Rose et al. 1978; Peterson and Rose 1985; Rose 1987), the Aleutians (Kay and Kay 1985), the weakly-alkalic HAB of Bogoslof Island also in the Aleutians (Byers 1959, 1961; Arculus et al. 1977), and Kick'em-Jenny volcano in the Lesser Antilles (Sigurdsson and Shepherd 1974). Therefore, it appears inescapable that at least some HABs have high initial H_2O contents.

Eruptive styles also suggest high volatile contents; many HABs and BAs are erupted as scoria, and block and ash flows, as well as lavas. The pyroclastic deposits and flows make up mafic to intermediate stratovolcanos such as Fuji in Japan (Aramaki and Ui 1978). Volatile effervescence powers the pyroclastic basalt and basaltic andesite eruptions. As White and Waring (1963) and more recent workers (e.g., Quisefit et al. 1989) document, the dominant volatile released at arc volcanos is H_2O .

Aluminous gabbros and diorites of continental margin batholiths show some of the clearest evidence for high magmatic H_2O contents, likely because they solidified at pressures too high for significant degassing prior to crystallization. These rocks contain very Ca-rich plagioclase and abundant hornblende, and hornblende-plagioclase pegmatites of basaltic composition are common. Examples of hydrous mafic intrusives can be found in the Sierra Nevada, California (Sisson 1991), the Adamello Massif, Italy (Ulmer et al. 1983; Blundy and Sparks 1992), the Peninsular Ranges batholith, southern California and Mexico (Walawender 1976; Walawender and Smith 1980; Smith et al. 1983), the Tertiary plutons of Washington State (C.A. Hopson personal communication), and the Coastal batholith of Peru (Pitcher et al. 1985). The geologic evidence is consistent with high H_2O contents in many HABs and BAs and has prompted us to investigate the phase relations of HABs in the presence of H_2O fluid.

Experimental approach, techniques and results

We conducted H_2O -saturated melting experiments at 1 kb pressure to develop methods for estimating the temperatures and H_2O contents of HABs. The results of the 1 kb experiments are presented in this study and are used with the 2 kb results of Sisson and Grove (1992) and anhydrous experimental data from the literature to infer the origins, crystallization behaviors, temperatures, and H_2O contents of common low-MgO HABs and BAs.

Starting materials and experimental techniques

Experiments at 1 kb pressure were performed on powdered volcanic rocks: magnesian HAB 79–35 g (9.86 wt.% MgO), a more evolved

HAB 82-66 (7.47 wt.% MgO), and an andesite inclusion 1140 Mf (4.47 wt.% MgO) from a rhyolite glass flow (Grove and Donnelly-Nolan 1986), plus excess H₂O. All of the samples were collected from Medicine Lake volcano, California, and phase relations of samples 79-35 g and 82-66 were investigated by Sisson and Grove (1992) at 2 kb and H₂O-saturated. Analyses of starting materials are presented in Table 2.

The experimental techniques are presented in Sisson and Grove (1992). Briefly, powdered samples plus H₂O were contained in crimped Au (Ag₇₀Pd₃₀ above 1060 °C) inner capsules within welded Au (Au₈₀Pt₂₀ above 1060 °C) outer capsules that also contained an NNO buffer assemblage plus additional H₂O. Experiments were performed in TZM or MHZ vessels pressurized with mixed Ar and CH₄ and quenched with a rapid method that nearly eliminates growth of quench crystals. Phase compositions were determined by wavelength-dispersive electron microprobe techniques shown by Sisson and Grove (1992) to be adequate for the analysis of hydrous mafic glasses. Saturation H₂O contents of representative experimental glasses produced at 1 and 2 kb were measured by J. Dixon at the California Institute of Technology using FTIR techniques similar to those described by Silver and Stolper (1989).

Experimental temperatures, phase assemblages, and phase proportions are reported in Table 3. Phase compositions are reported in Table 4. Melt H₂O contents are presented in Table 5. Phase proportions have been calculated from mass balance relations among bulk composition (Table 2) and phase compositions (Table 4) using a least squares technique incorporating analytical uncertainties (Albarede and Provost 1977). Iron lost from the samples to Au or Ag₇₀Pd₃₀, estimated from mass balance calculations, is < 10 % (relative) of the total Fe contained in the starting materials. Thus, we conclude that bulk compositions were maintained acceptably and that the experimental results can be used in interpreting the petrogenesis of HAB magmas.

Experimental results

Liquids. Experimental liquids produced by melting of H₂O-saturated HABs at 1 kb coexist with olivine and spinel or olivine, high-Ca pyroxene, and plagioclase and range in composition from low-MgO HAB to typical arc andesite (Table 4). The small number of 1-kb results precludes discussion of differentiation trends.

Pyroxene. Synthesized pyroxenes are magnesian calcic augite or diopside (Fig. 1). Pyroxene crystal rims have somewhat heterogeneous compositions with more aluminous regions also being more Fe-rich and Ca-poor. Low-alumina regions are more abundant and with coexisting melt describe an average exchange $K_D^{Fe-Mg} (= (Fe/Mg)_{cpx}/(Fe/Mg)_{liq})$ of 0.22 (± 0.04 , 2- σ , using total Fe), comparable to results at 2 kb H₂O-saturated (Sisson and Grove 1992) and 1 atm anhydrous (Grove and Bryan 1983).

Olivine. Iron and magnesium are partitioned between olivine and liquid with an average $K_D^{Fe-Mg} (= (Fe/Mg)_{oliv}/(Fe/Mg)_{liq})$ of 0.29 (± 0.03 , 2- σ , using total Fe). Sisson and Grove (1992) present Fe³⁺/total Fe measured by Mössbauer spectroscopy of 0.137 for HAB melt saturated with H₂O at 2 kb, NNO-buffered. Applying this to our 1 kb results gives $K_D^{Fe^{2+}-Mg}$ of 0.34, within the range (0.26-0.36) used by Roeder and Emslie (1970) to define the commonly accepted K_D^{Fe-Mg} between olivine and basaltic liquid of 0.30.

Table 2. Compositions of starting materials

Sample	SiO ₂	Al ₂ O ₃	FeO*	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO	Total
79-35 g	48.2	18.2	8.39	9.86	12.01	2.29	0.09	0.66	0.05	0.16	99.91
82-66	51.2	17.3	8.66	7.47	10.21	3.11	0.70	1.01	0.16	0.16	99.98
1140 mf	56.9	17.6	7.25	4.47	7.97	3.58	1.27	0.96	0.16	0.15	100.31

Analyses by XRF, U. Mass., Amherst. M.B. Baker-analyst. Analyses of 79-35 g and 82-66 recalculated from Baker (1988)

Table 3. Experimental conditions and products. See Table 4 for phase compositions. All experiments at 1 kb pressure, $P_{H_2O} = P_{total} fO_2$ buffered at NNO

Run #	T °C	Time (hours)	Phases (% ^a) + vapor	+/- FeO ^b	+/- FeO ^c	Capsule
79-35 g-						
#17	1100	15	gl(94), ol(6), sp(< 1)	- 0.7	0.0	Ag ₇₀ Pd ₃₀
#16	1082	10	gl(60), ol(13), pl(22), cpx(5)	- 1.4	- 5.2	Ag ₇₀ Pd ₃₀
82-66-						
#10	1050	23	gl(86), ol(8), pl(5), cpx(< 1)	- 1.5	- 6.8	Au
#9	1035	24	gl(68), ol(9), pl(15), cpx(9)	- 1.2	- 8.1	Au
#8	1020	18	gl(60), ol(11), pl(21), cpx(9)	- 0.9	- 5.9	Au
1140MF-						
#18	1050	9	gl(99), ol(1)	- 1.6	- 1.5	Au

^a Proportions calculated by mass balance incorporating analytical errors (Albarede and Provost 1977) for phase compositions with all Fe as FeO and ignoring MnO and P₂O₅. Proportions are precise to 5% relative or better for abundance > 20%, ~10% at abundances 10-20%, ~ 20% at abundances of 1-10%, and ~ 50% at abundances < 1%.

^b Apparent loss of FeO expressed as: $100 * (total\ FeO_{calc.} - total\ FeO_{st.material}) / total\ FeO_{st.material}$

^c Apparent loss of FeO estimated by including a fictive pure FeO phase in regression, reported as -percent fictive FeO/total FeO_{st.material}

Table 4. Electron microprobe analyses of experimental phases. See Table 3 for conditions

Run # Phase	SiO	Al ₂ O ₃	FeO	MgO	CaO	TiO ₂	MnO	Na ₂ O	K ₂ O	P ₂ O ₅	Cr ₂ O ₃	Total
79-35g# - 17												
gl(9)	48.7(2)	19.0(1)	8.20(12)	7.87(9)	12.6(1)	0.63(3)	0.14(3)	2.62(9)	0.10(2)	0.15(2)	0	94.7
ol(4)	40.1(2)	0.03(1)	13.8(5)	46.2(4)	0.38(3)	0.03(1)	0.22(2)				0	100.8
sp(3)		44.3(8)	18.4(1)	17.4(2)	0.25(2)	0.33(6)	0.23(3)				20.8(8)	101.7
# 16												
gl(10)	51.1(2)	17.5(2)	8.91(15)	6.09(22)	11.5(3)	0.93(4)	0.18(5)	3.53(13)	0.17(1)	0.15(2)	0	94.5
ol(4)	39.4(6)	0.07(1)	17.8(8)	41.9(9)	0.47(6)	0.05(3)	0.31(3)				0.08(2)	100.1
cp(9)	51.5(7)	3.7(6)	5.18(36)	15.8(5)	22.8(3)	0.5(1)	0.09(3)	0.24(3)			0.66(12)	100.4
pl(7)	46.9(6)	33.0(5)	0.72(6)	0.2(1)	17.2(4)			1.67(18)	0.02(1)			99.8
82-66-# 10												
gl(10)	53.2(5)	17.7(2)	8.12(8)	5.03(13)	10.0(2)	1.18(2)	0.14(4)	3.53(14)	0.87(3)	0.23(3)	0	94.8
ol(4)	38.9(2)	0.04(1)	19.2(2)	41.8(6)	0.40(1)	0	0.24(3)				0	100.6
cp(10)	52.1(3)	3.0(2)	5.60(32)	16.4(2)	21.9(2)	0.60(4)	0.11(3)	0.22(2)			0.50(5)	100.4
pl(8)	47.4(6)	33.2(3)	0.66(4)	0.17(2)	16.7(5)			1.81(23)	0.04(1)			100.0
# 9												
gl(10)	54.8(2)	17.5(1)	8.10(9)	4.14(5)	8.51(9)	1.38(3)	0.17(2)	4.01(15)	1.09(3)	0.24(3)	0	95.4
ol(5)	38.4(5)	0.04(1)	21.8(4)	39.3(8)	0.36(4)	0.04(1)	0.36(3)				0.03(1)	100.4
cp(11)	51.8(4)	3.2(3)	7.1(8)	15.6(3)	21.6(6)	0.8(1)	0.17(3)	0.27(3)			0.24(11)	100.8
pl(13)	48.4(4)	32.4(5)	0.77(7)	0.18(7)	16.2(4)			2.26(23)	0.08(2)			100.3
# 8												
gl(7)	55.8(2)	17.4(1)	8.24(14)	3.45(5)	7.71(21)	1.49(5)	0.18(2)	4.18(11)	1.23(4)	0.27(2)	0	94.9
ol(4)	38.1(2)	0.05(1)	24.2(6)	37.3(4)	0.37(3)	0.03(1)	0.41(6)				0	100.5
cp(19)	51.8(6)	3.0(5)	7.15(42)	15.6(4)	21.6(6)	0.77(15)	0.20(3)	0.25(5)			0.16(12)	100.6
pl(9)	48.5(6)	32.6(3)	0.72(4)	0.11(2)	16.2(4)			2.25(17)	0.08(1)			100.5
1140MF-# 18												
gl(8)	57.2(5)	17.5(3)	6.81(22)	4.26(11)	7.86(18)	0.94(2)	0.11(5)	3.80(16)	1.30(6)	0.22(3)	0	94.7
ol(4)	39.3(5)	0.04(2)	20.2(4)	40.2(9)	0.24(1)	0.04(1)	0.31(3)					100.3

gl-glass, ol-olivine, sp-spinel, cp-clinopyroxene, pl-plagioclase. Numbers in parentheses following phase designations are the number of replicate measurements averaged to obtain the reported analysis. Numbers in parentheses following oxide concentrations are one standard deviation of the average for that oxide and have units of the least significant digits reported. Thus, 6.81(22) is read as 6.81 ± 0.22. Glass analyses normalized to 100%; original total reported. Blank-not analyzed, 0-below detection

Table 5. H₂O contents of experimental liquids

Sample	wt.% SiO ₂	T °C	P kb	H ₂ O FTIR	H ₂ O*	H ₂ O**
1140MF-# 18	57.2	1054	1	3.76 ± 0.21	3.84	4.00
87S35A-# 14	51.9	1058	2	5.94 ± 0.17	6.26	5.81
81-T-116 (matrix)	55.8	1050	2	6.17 ± 0.02	6.27	5.84

Notes: Samples 87S35A-# 14 and 81-T-116 (matrix) are a fused hornblende HAB dike and the fused matrix of a hornblende HAB. An analysis of 87S35A is presented in Table 1. An analysis of 81-T-116 (matrix) is provided by Sisson and Grove (1992)
H₂O* and H₂O** are H₂O solubilities calculated by the techniques of Burnham (1979) and Housh and Luhr (1991) respectively

Plagioclase. Exchange of Ca and Na between plagioclase and basaltic or andesitic liquid can be expressed in terms of the exchange K_D^{Ca-Na} , defined as (Ca/Na) plag/(Ca/Na) liq. At 1 kb, H₂O-saturated (approximately 3.8 wt. % H₂O in melt) the average exchange K_D^{Ca-Na} is 3.4 (± 0.6, 2-σ). This compares to a K_D^{Ca-Na} of ~ 5.5 for melts with 6 wt. % H₂O (Sisson and Grove 1992), about 1.7 for basaltic and andesitic melts with 1.8 wt. % H₂O (Baker and Egger 1987), and 1.0 for anhydrous basaltic melts at pressures below 10 kb (data summarized in Sisson and Grove 1992).

Discussion

Application of 1 and 2 kb experiments to volcanic rocks

Aleutians. Basalts or basaltic andesites with Al₂O₃ ≥ 19 wt.% and MgO ≤ 5.5 wt.% (low-MgO HABs and BAs) are the most common magmas erupted from Aleutian volcanos (Marsh 1982). Most low-MgO HABs or BAs of the Aleutians carry a phenocryst assemblage of abundant plagioclase and lesser olivine, magnetite, and high-Ca

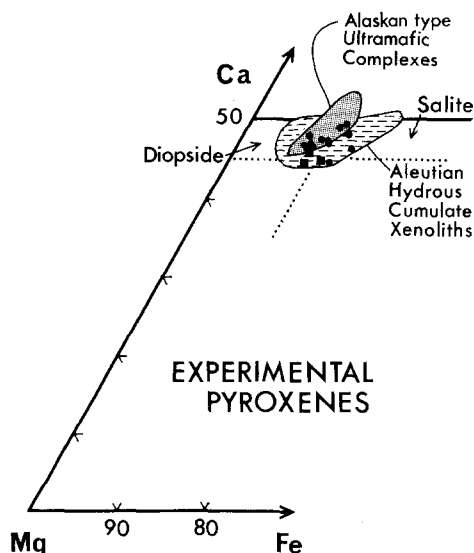


Fig. 1. Relative molar proportions of Ca, Mg, and Fe in synthetic high-Ca pyroxenes produced at 1 and 2 kb (Sisson and Grove 1992) H_2O -saturated (squares and dots). Synthetic pyroxenes are diopside, salite, or calcic augite (classification of Poldervaart and Hess 1951). Comparable pyroxenes are found in Alaskan-type ultramafic complexes (shaded area) and in hornblende-bearing cumulates erupted as xenoliths in the Aleutians (horizontal ruled area) (fields after Conrad et al. 1983; Conrad and Kay 1984)

pyroxene. In the few cases where the composition of the plagioclase has been reported (Byers 1961; Brophy 1986; Marsh et al. 1990; Singer et al. 1992; Kay and Kay 1992), calcic plagioclase ($An_{80} - An_{96}$) is present. Hornblende or low-Ca pyroxene phenocrysts are present in BAs at some volcanic centers (Kay and Kay 1985), but are comparatively rare.

Aleutian HAB and BA whole-rock analyses resemble the compositions of 2-kb experimental liquids saturated with H_2O , olivine, Ca-plagioclase, and either high-Ca pyroxene or hornblende (with and without magnetite) (Table 1). Accordingly, the Aleutian HABs and BAs coincide with the 2-kb olivine plus Ca-plagioclase plus pyroxene or hornblende (plus aqueous fluid and with or without spinel)-saturated liquids in pseudo-ternary projections (Fig. 2). The experimental 2-kb melts contain approximately 6 wt.% H_2O , calculated by the method of Burnham (1979). The similarity in the compositions of wet experimental liquids and natural lavas and the presence of the same saturating minerals suggests that most Aleutian HABs were once multiply-saturated liquids with several or more wt.% dissolved H_2O . This conclusion is supported by the experimental results of Baker and Egglar (1983, their Fig. 3), which show that, within experimental brackets, a typical Aleutian HAB has plagioclase, olivine, oxides, and either high-Ca pyroxene or hornblende together on its liquidus at 2 kb and 4–6 wt.% dissolved H_2O .

Phenocryst compositions support the interpretation that Aleutian HABs and BAs were multiply-saturated H_2O -rich liquids prior to eruption. Brophy (1986) presents whole-rock and phenocryst core compositions for seven HABs from the Cold Bay volcanic center of the

Aleutian arc. The range of plagioclase and olivine phenocryst core compositions can be reproduced using experimentally determined 2-kb H_2O -saturated Ca-Na and Fe-Mg exchange K_D s if the whole rock compositions are used as the liquids from which the phenocryst cores grew (Fig. 3). Plagioclase compositions cannot be reproduced using exchange K_D^{Ca-Na} for dry conditions (approximately 1 from 1 atm up to 10 kb, Sisson and Grove 1992) using either whole-rock or matrix compositions (from Crawford et al. 1987) as liquids. Exchange K_D s determined for andesite melts with low H_2O contents (about 1.8 wt.% H_2O , K_D 1.3–2.0; Baker and Egglar 1987) also fail to produce the observed plagioclase phenocryst compositions. The estimated high H_2O contents are consistent with Burnham's thermodynamic model of plagioclase-hydrous melt equilibria (Burnham 1981) as applied by Marsh et al. (1990) to Aleutian magmas.

The high-Ca pyroxene phenocryst cores in Cold Bay HABs are moderately aluminous (average 3.6 wt.% calcic augite and salite (average 20.4 wt.% CaO), close in composition to both 1 and 2-kb H_2O -saturated experimental pyroxenes (average 4.5 wt.% Al_2O_3 , 22.5 wt.% CaO) and 1-atm pyroxenes (average Al_2O_3 2.5 wt. %, 20.5 wt.% CaO) that coexist with basalt or basaltic andesite melts (Grove et al. 1982; Baker and Egglar 1987; Sisson and Grove 1992). Kay and Kay (1985) present comparable HAB and BA pyroxene analyses (average Al_2O_3 2.7 wt.%, average CaO 20.6 wt. %) in a regional study of Aleutian mafic phenocrysts. The natural pyroxenes are distinctly more calcic and less aluminous than pyroxenes grown from anhydrous HAB melts at high pressures (average 8–30 kb anhydrous: 9.7 wt.% Al_2O_3 , 15.1 wt. % CaO; Johnston 1986; Baker and Egglar 1987; Bartels et al. 1991). This observation suggests that the Aleutian phenocryst assemblage does not result from high pressure anhydrous crystallization. The agreement between whole rocks and multiply-saturated wet liquid compositions, and of phenocryst cores (notably plagioclase) and predicted or experimentally produced compositions assuming that whole rocks were wet liquids, supports the notion that Aleutian low-MgO HABs and BAs were once multiply-saturated liquids that contained at least 4 and likely as much as 6 wt. % H_2O .

The characteristic abundance of phenocrysts in Aleutian (and other) HABs and BAs is consistent with a model of shallow degassing and reequilibration prior to eruption. H_2O -rich magmas will saturate with aqueous fluid as they ascend to the surface. Aleutian HAB liquids with about 4–6 wt.% H_2O would saturate with aqueous fluid at approximately 3–6 km depth. Magmas that ascend to lower pressures will exsolve H_2O into fluid and then vapor and the liquids will follow a saturation curve, becoming drier with continued ascent. Crystals, chiefly plagioclase, will grow as the liquids desiccate and multiple saturation boundaries shift toward 1-atm positions and temperatures. The near absence of hornblende phenocrysts in Aleutian HABs and BAs likely results from inappropriate bulk compositions (insufficient Na_2O , Sisson and Grove 1992) or possible breakdown at shallow depths, prior to eruption.

The high H_2O contents inferred for Aleutian (and other) low-MgO HABs could be produced by extensive

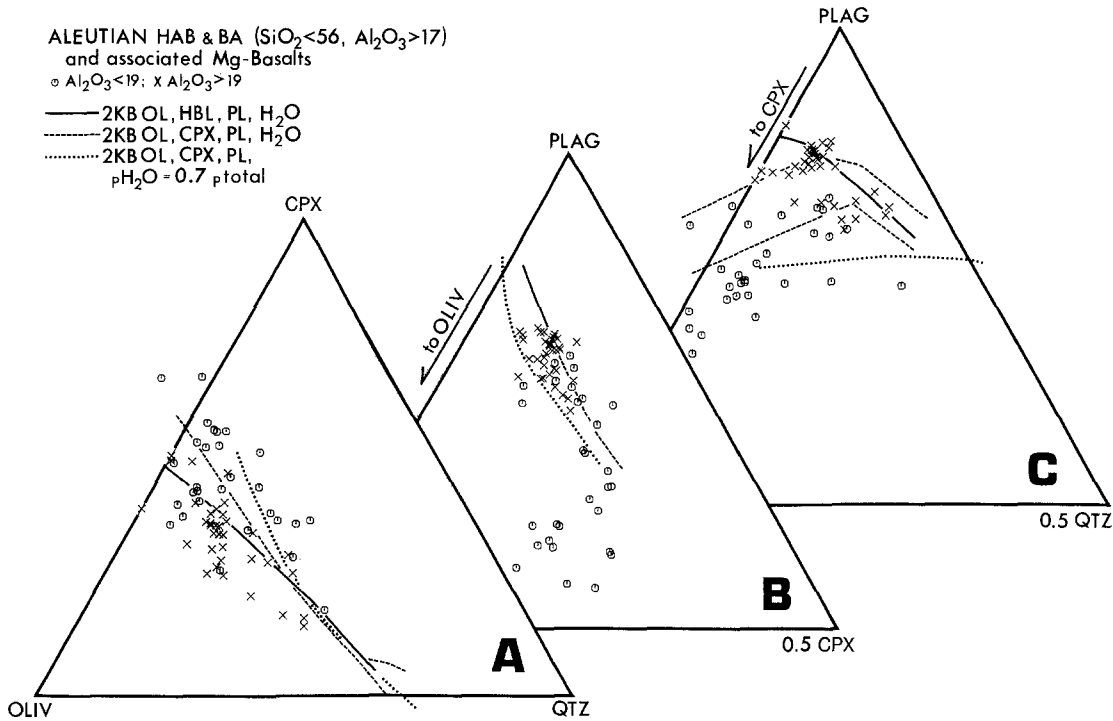


Fig. 2A–C. Comparison of HABs, BAs, and associated MgO-rich basalts from the Aleutian arc with multiple saturation boundaries at moderate and high melt H₂O contents. Rock analyses from Marsh (1976, 1982), Kay and Kay (1985), Brophy (1986), Myers et al. (1986), Nye and Reid (1986), Debari et al. (1987), and Gust and Perfit (1987). Saturation boundaries from Sisson and Grove (1992) and Spulber and Rutherford (1983). Projection scheme from Torrey

et al. (1987) uses oxygen units and projects from apatite, orthoclase, and an oxide with Fe₂O₃ in liquids estimated with the expression of Kilinc et al. (1983) at the NNO buffer. Rocks are divided into compositions with greater or less than 19 wt.% Al₂O₃ for clarity of presentation. **A** Subprojection from PLAG (An plus Ab). **B** Subprojection from QTZ. **C** Subprojection from OLIV (Fo plus Fa)

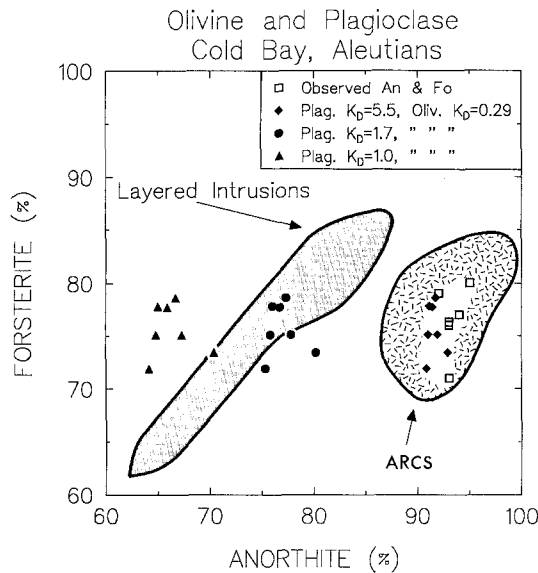


Fig. 3. Calculated and observed compositions of olivine and plagioclase phenocryst cores for HABs from the Cold Bay volcanic center, Aleutians (Brophy 1986). Fields for minerals from arc intrusives, cumulate inclusions, and volcanics (ARCS) and continental layered intrusions are after Arculus and Wills (1980) and Beard and Borgia (1989)

crystallization-differentiation of lower-H₂O mantle-derived magmas. Aleutian HABs are associated with less abundant basalts with higher MgO and lower Al₂O₃. Kay

et al. (1982), Nye and Reid (1986), and Gust and Perfit (1987) have proposed that these high-MgO basalts are parental to the HAB and BA suite. Gust and Perfit (1987) investigated this hypothesis with anhydrous experiments at 8 kb on one of the high-MgO Aleutian basalts and showed that the composition crystallizes olivine followed by olivine plus high-Ca pyroxene, and that prior to plagioclase saturation the liquid is progressively enriched in Al₂O₃ and depleted in MgO. Their starting composition and 8 kb experimental liquids are shown in Fig. 4, projected from QTZ onto the OLIV-CPX-PLAG pseudoternary (mineral components in oxygen units where OLIV is Fo plus Fa, CPX is Di plus Hd, and PLAG is An plus Ab). Also shown is the field defined by Aleutian HABs, BAs, and associated high-MgO lavas, including the starting composition of Gust and Perfit (1987). Gust and Perfit (1987) conclude that extensive crystallization of olivine and high-Ca pyroxene (with or without spinel) is required to produce HAB from high-MgO low-Al₂O₃ basalt. The dry experimental liquids do not, however, follow the field defined by the Aleutian magma series (Fig. 4). The Aleutian magmas likely crystallized under wetter conditions in which the olivine primary phase volume was expanded relative to that in the dry experiments.

The H₂O contents of parental and potentially primary high-MgO basalts are important for models of arc magma genesis and can be estimated by crystal fractionation calculations that result in low-MgO HAB compositions and that reproduce the trends defined by the Aleutian

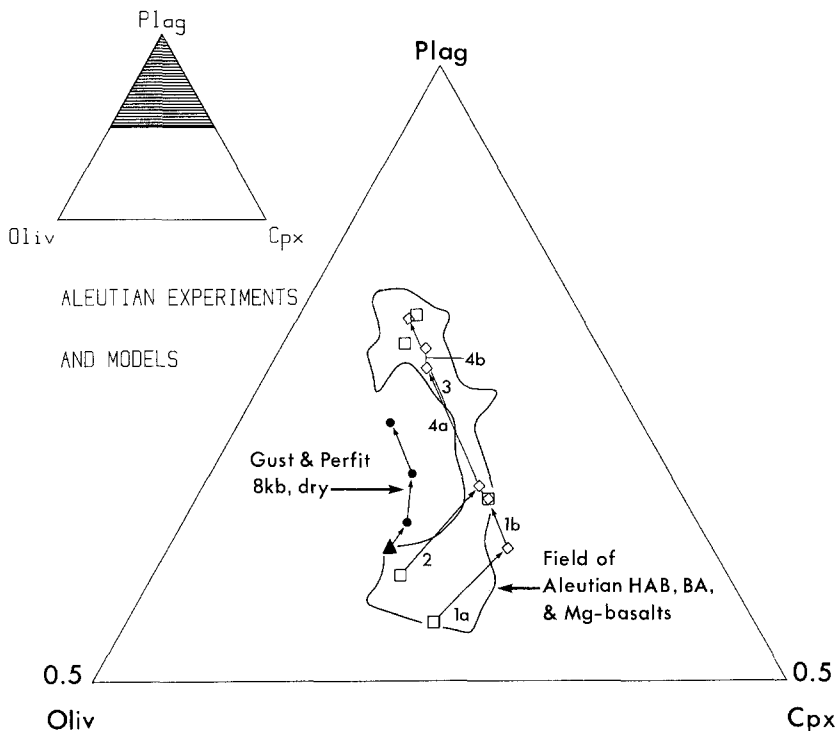


Fig. 4. Pseudo-ternary projection from QTZ of crystal fractionation models (Table 6) constructed to match the Aleutian magma series (outlined from Fig. 2b, see also Fig. 5). *Solid dots* show successively lower temperature liquids produced at 8 kb, anhydrous from an MgO-rich Aleutian basalt (starting composition is triangle) by Gust and Perfit (1987). *Models 1a* olivine fractionation from Mg-basalt host for ultramafic xenoliths (*square*, Adak basalt from Debari et al. 1987) to $Mg \#_{liq} = 62.5$ (*diamond*), followed by *1b*, crystallization of olivine plus high-Ca pyroxene to reach target HAB OK2 (*square*, model is coincident diamond; Okmok HAB from Nye and Reid 1986). *2* Crystallization of olivine from Mg-basalt ID16 (*square*, Okmok basalt from Nye and Reid 1986) to reach target HAB OK2 (*square*, model is adjacent diamond). *3* Crystallization of olivine plus high-Ca pyroxene from HAB OK2 to reach average Atka HAB (*square* closest to PLAG apex, model is overlapping diamond; Atka average from Myers et al. 1986). *4a* Crystallization olivine plus high-Ca pyroxene plus magnetite from HAB OK2 to $Al_2O_3^{liq} = 19.8$ wt.% (*diamond*), followed by *4b*, cotectic crystallization of olivine plus high-Ca pyroxene plus plagioclase plus magnetite to reach average Cold Bay HAB (*square*, model is adjacent diamond; average Cold Bay HAB from Brophy 1986)

magma series. Results of forward models that successfully relate high-MgO Aleutian basalts to low-MgO HABs using reasonable phase assemblages and phase compositions are presented in Table 6 and are illustrated in Figs. 4 and 5. To summarize, high-MgO basalt crystallizes approximately 10 wt.% olivine (perhaps accompanied by minor spinel) yielding moderate-MgO HAB. Moderate-MgO HAB crystallizes olivine plus high-Ca pyroxene (possibly with minor spinel) in proportions of about 0.15:0.85 (equilibrium relative proportions at 2 kb H_2O -saturated, Sisson and Grove 1992) either directly yielding low-MgO HAB or giving way to cotectic olivine plus high-Ca pyroxene plus plagioclase crystallization. Typical low-MgO HABs of the Aleutians are the residual liquids left after 30–40 % solidification of some Aleutian high-MgO basalts (Table 6). Conrad and Kay (1984) present a similar open-system crystallization model and infer 21–33 % solidification. If low-MgO HABs contained 4–6 wt.% H_2O , as indicated by the experiments of Baker and Egger (1983), Sisson and Grove (1992), and this study, our crystallization model suggests that parental Aleutian high-MgO basalts contained approximately 2.5–4.5 wt.% H_2O . These predicted H_2O contents are approached by primitive back-arc basin basalts quenched at seafloor pressures (up to about 2.3 wt.%, Muenow et al. 1990; Stolper and Newman 1992). We conclude that the comparable to somewhat higher H_2O contents predicted here for parental arc basalts are plausible considering the H_2O measured in arc-related back-arc basin basalts. *Guatemala*. Low-MgO HABs and BAs are erupted

throughout the length of the active volcanic arc in Central America (Carr and Stoiber 1988). The compositions of these lavas and scoria are similar to those erupted in the Aleutians (Table 1). Carr et al. (1982) show that Guatemalan HABs have the greatest Na_2O contents of mafic Central American lavas, with an average of about 3.7 wt.% Na_2O at 52 wt.% SiO_2 . Sisson and Grove (1992) have shown that high Na_2O promotes early formation of hornblende from wet low-MgO HAB liquids.

The geologic evidence of high H_2O contents in the Guatemalan HABs and BAs is unequivocal. Hornblende has been recognized in HABs or BAs at the Fuego, Santa Maria, Atitlan, and Ayarza volcanic centers (Rose et al. 1978; Rose 1987; Rose et al. 1987; Peterson and Rose 1985). Hornblende phenocrysts are best preserved in HAB or BA scoria erupted in association with more silicic pumice. Hornblende is resorbed or is preserved only as inclusions in other phenocrysts in other HAB eruptions (Rose et al. 1978). Hornblende is absent in low-MgO HAB and BA from volcanos in El Salvador, Costa Rica, and Nicaragua (M. Carr, written communication 1989), regions where average Na_2O is lower than in Guatemala. Calcic plagioclase is also present (up to An_{97} , Anderson 1984) in Guatemalan HABs.

Fuego, in Guatemala, is one of the most active stratovolcanos on Earth (Martin and Rose 1981). Eruptive products range from magnesian HAB (very rare) to silicic andesite (including corundum-normative andesites), but are overwhelmingly dominated by low-MgO HAB and BA (Chesner and Rose 1984; CENTAM data base-Carr

Table 6. Aleutian fractionation models

High-MgO basalt to high-alumina basalt									
Parent: basaltic host for ultramafic xenoliths, Adak Island (Debari et al. 1987).									
SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	
48.7	0.69	15.2	9.08	11.89	11.43	2.09	0.74	0.10 ^a	
Crystallizing assemblage: 100% oliv ^b to Mg# _{liq} = 62.5, followed by 15% oliv + 85% Ca-pyx ^b .									
Target composition: HAB OK2, Okmok Volcano (Nye and Reid 1986).									
50.2	0.83	17.4	9.00	7.12	12.13	2.54	0.57	0.12	
Model after 15.7% crystallization:									
49.6	0.79	17.8	8.96	7.22	12.17	2.47	0.88	0.12	
Parent: magnesian basalt ID 16, Okmok Volcano (Nye and Reid 1986).									
49.1	0.70	16.1	8.93	11.45	10.92	2.21	0.52	0.12	
Crystallizing assemblage: 100% oliv.									
Target composition: HAB OK2 (as above).									
Model after 10.5% crystallization:									
50.1	0.78	17.9	8.50	7.29	12.20	2.47	0.58	0.13	
High-alumina basalt to low-MgO high-alumina basalt									
Parent: HAB OK2 (as above).									
Crystallizing assemblage: 15% oliv + 85% Ca-pyx.									
Target composition: Average HAB, Atka Island (Myers et al. 1986).									
50.7	0.91	20.9	9.28	3.70	10.31	3.28	0.71	0.16	
Model after 19% crystallization:									
50.5	0.93	21.0	9.28	3.97	10.34	3.16	0.72	0.15	
Parent: HAB OK2 (as above).									
Crystallizing assemblage: 8% oliv + 86% Ca-pyx + 6% magnetite ^b to 19.8 wt.% Al ₂ O _{3liq} , followed by 7% oliv + 37% Ca-pyx + 48% Ca-plag ^b + 8% magnetite (2-kb cotectic proportions, H ₂ O-saturated, Sisson and Grove 1992).									
Target composition: Average HAB, Cold Bay volcanic center (Brophy 1986).									
52.1	0.96	19.7	8.75	4.46	10.01	2.80	0.77	0.17	
Model after 26% crystallization:									
51.7	0.95	19.8	8.72	4.64	9.92	3.31	0.77	0.16	
Total solidification high-MgO basalt to low-MgO HAB: 28–38%									

^a Assumed concentration for modeling purposes.

^b Mineral compositions and exchange K_Ds from 2-kb experiments on HAB 79–35 g (Sisson and Grove 1992)

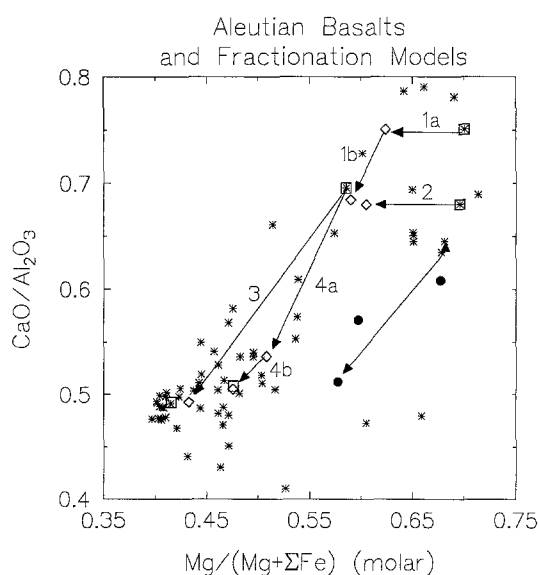


Fig. 5. Aleutian HABs, BAs, and MgO-rich basalts (stars) and crystal fractionation models (Table 6). Model designations and analytical references as in Fig. 4. Starting composition and 8-kb experimental liquids of Gust and Perfit (1987) are shown as triangle and circles

and Rose 1987). Rose et al. (1978) provide a comprehensive description of the October 1974 eruption and eruptive products of Fuego. The weighted average October 1974 Fuego magma was low-MgO plagioclase-porphyrific HAB (Table 1). Phenocryst-free groundmass separates of October 1974 scoria are low-MgO high-alumina BA (Table 1), close to the average composition of glass inclusions in phenocrysts from the 1974 eruption. Rose et al. (1978) interpret low totals of glass inclusion analyses as evidence of approximately 4 wt.% H₂O in the parent magma and Harris and Anderson (1984) obtained 1.5–3.4 wt.% H₂O by vacuum fusion of six large HAB glass inclusions from the 1974 eruption.

Eruptive products of Fuego are plotted in Fig. 6. Like Aleutian HABs, the Guatemalan rocks plot coincident with the 2-kb experimental liquids saturated with aqueous fluid, olivine, Ca-plagioclase, and hornblende or high-Ca pyroxene (with and without magnetite). The agreement between experimental wet, multiply-saturated liquids and natural low-MgO HABs and BAs is taken, as with the Aleutians, as evidence that most of the magmas were once multiply-saturated hydrous liquids. Rose et al (1978) argue that the magmas have partly degassed and have grown their phenocrysts prior to eruption.

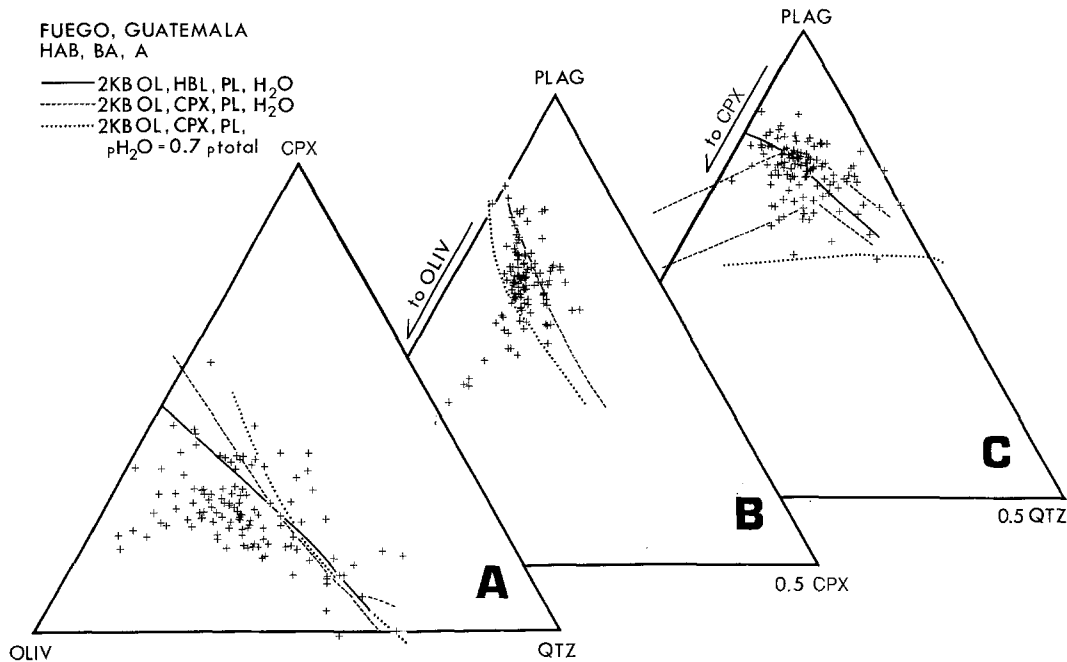


Fig. 6A–C. Eruptive materials from Fuego, Guatemala (crosses, CENTAM data base, Carr and Rose 1987) compared with experimental multiple saturation boundaries at moderate-to-high H₂O contents of melts (Sisson and Grove 1992; Spulber and Rutherford

1983). Projection as in Fig. 4. Fuego compositions range from HAB to minor corundum normative aluminous andesite. No compositions have Al₂O₃ < 18 wt.%. **A** Projection from PLAG. **B** Projection from QTZ. **C** Projection from OLIV

Application to plutonic rocks

Alaskan-type ultramafic complexes and Aleutian cumulate xenoliths. The crystal fractionation model developed for Aleutian magmas also predicts a cumulate rock series similar to that observed in both Alaskan-type ultramafic complexes (Irvine 1974) and in hydrous mineral-bearing xenoliths erupted in lavas of the Aleutians (Conrad and Kay 1984; Conrad et al. 1983; Debari et al. 1987). Conrad and Kay (1984) and coworkers (mentioned already) also argue for a characteristic cumulate series resulting from differentiation of high-MgO basalts to HABs and note that this series is exposed in Alaskan-type ultramafic complexes. Cumulates produced during crystal fractionation of parental Aleutian high-MgO basalt to form low-MgO HAB can be inferred from Fig. 4 and Table 6. Parental magmas will first precipitate olivine (perhaps accompanied by minor spinel) leaving dunites. The following high-Ca pyroxene plus olivine fractionation interval leaves olivine clinopyroxenite or wehrlite (also potentially spinel-bearing). Eventually plagioclase joins olivine and high-Ca pyroxene, leaving olivine gabbro cumulates. Gabbros would be characterized by very Ca-rich plagioclase. Cumulus olivine and pyroxene would, in many cases, be partly consumed by reaction with intercumulus liquid to produce hornblende. Alaskan-type ultramafic complexes are made up of the predicted cumulate association (Irvine 1974) of dunite, olivine clinopyroxenite and wehrlite, and hornblende-bearing gabbro. Undeformed cumulate xenoliths from the Aleutians include olivine clinopyroxenites (with or without abundant cumulus hornblende), hornblende gabbros, and anhydrous orthopyroxene gabbros. Deformed cumulate xenoliths also in-

clude dunites and wehrlites (Debari et al. 1987). Pyroxenes in Alaskan-type ultramafic complexes and in Aleutian hydrous cumulate xenoliths are aluminous diopsides and salites, similar to the experimental pyroxenes produced at 2 kb H₂O-saturated conditions by Sisson and Grove (1992) (Fig. 1) and experimental spinels overlap those of Alaskan-type complexes (Sisson and Grove 1992). The agreement between modeled and observed cumulates and similar experimental and cumulus mineral compositions support the crystal fractionation model relating Aleutian high-MgO basalts to low-MgO HABs, is further evidence for high magmatic H₂O contents in many Aleutian basaltic magmas, and suggests a common crystallization sequence and high magmatic H₂O content in other older arcs.

Sierra Nevada batholith, California. The mafic intrusive rocks of the Mesozoic Sierra Nevada batholith, California, also provide evidence for high H₂O contents in HAB and BA magmas in an arc environment. Granodiorites and granites form the most common plutons of the batholith, but small intrusions of hornblende gabbro and diorite are also present. Swarms of thin mafic dikes or sills with aphyric textures provide samples of the mafic liquids present during growth of the batholith. The sills and dikes have compositions of low-MgO HAB, BA, and aluminous andesite (Sisson 1991). Na₂O contents are high, commonly 3.5–4.2 wt.%, and comparable to Guatemalan HABs. Early crystallization of hornblende and common miarolitic cavities are clear evidence of high magmatic H₂O contents. Compositions of sills from the Jurassic mafic intrusive complex at Onion Valley in the eastern Sierra Nevada are plotted in Fig. 7 (Sisson 1991). The sills lie along or near to the hornblende-olivine reaction

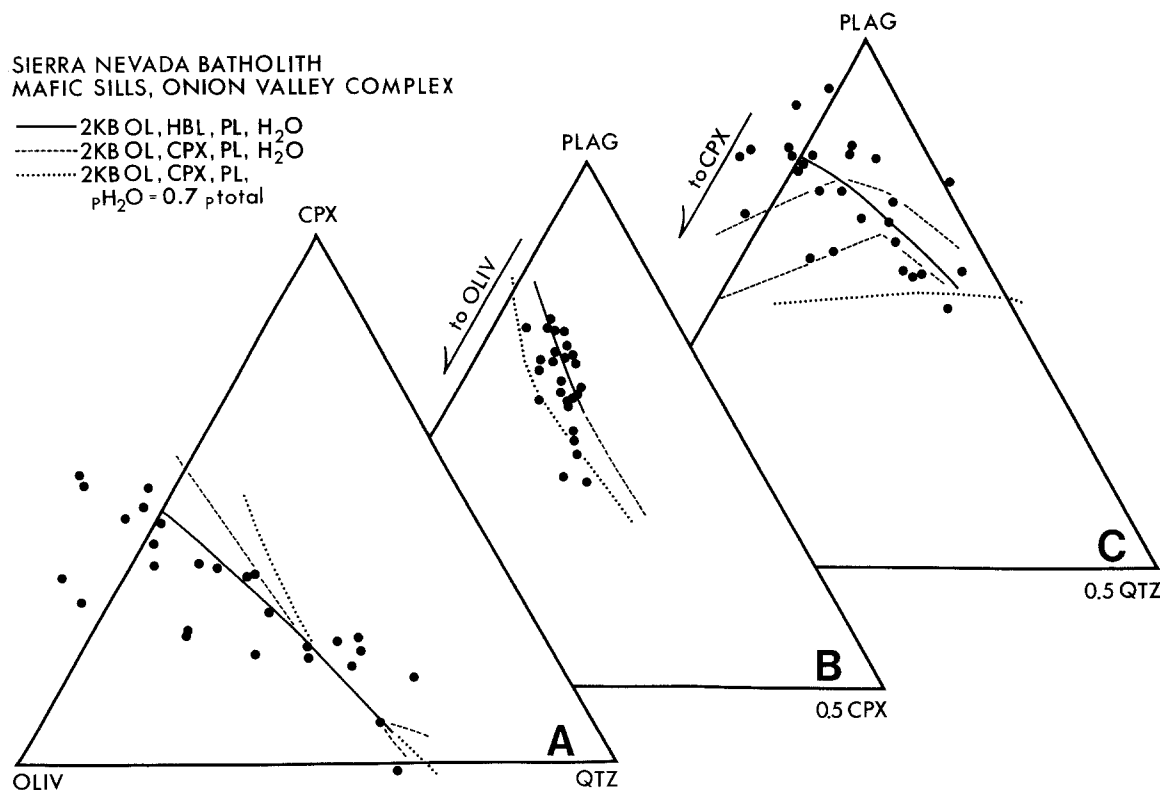


Fig. 7A–C. Mafic sills (hornblende gabbro and diorite) from the sheeted sill complex at Onion Valley, Sierra Nevada batholith (Sisson 1991), compared with the 2-kb H₂O-saturated olivine plus hornblende plus plagioclase plus liquid (with and without magnetite)

reaction boundary (Sisson and Grove 1992). 2-kb H₂O-saturated olivine-high-Ca pyroxene-plagioclase-liquid multiple saturation boundary shown for reference (*dotted*). A Projection from PLAG. B Projection from QTZ. C Projection from OLIV

boundary determined at 2-kb H₂O-saturated conditions by Sisson and Grove (1992), and likely preserve compositions of liquids controlled by that boundary. While the mafic sills are olivine-free, they are associated with olivine hornblende cumulates (olivine resorbed by hornblende) that formed as the sills solidified along the reaction boundary.

Geothermometry

A principle difference between an H₂O-rich and a dry silicate liquid saturated with the same solid phases is that the wet magma exists at a far lower temperature. A dry HAB liquid in equilibrium with olivine, high-Ca pyroxene, and plagioclase can exist at about 1170 °C at low to moderate pressures (Grove et al. 1982; Gust and Perfit 1987; Bartels et al. 1991). Basaltic liquid saturated with H₂O and the same solid phases is cooler by as much as 150 °C at 2 kb (Sisson and Grove 1992). In the following discussion, we have derived two geothermometers that can be used to estimate the temperatures of HABs and BAs. Successful development of both geothermometers has required estimates of the H₂O content of experimental liquids. Measured H₂O contents for HAB, BA, and andesite liquids at 1 or 2 kb are presented in Table 5 and are compared to saturation H₂O contents calculated for these liquids by the methods of Burnham (1979) and Housh and Luhr (1991). Note that the estimates of H₂O content

obtained by infrared measurements and those predicted by theory are in agreement. We have chosen to use the mean of the two infrared measurements weighted by the inverse of their uncertainties (6.15 wt.% H₂O) for the andesitic and basaltic liquids reported by Sisson and Grove (1992) at 2-kb H₂O-saturated. H₂O contents for 1-kb H₂O-saturated liquids of the present study, 2-kb rhyolite liquids of Sisson and Grove (1992), and the 5-kb H₂O-saturated diopside-anorthite piercing point (Yoder 1965) were calculated with Burnham's method.

Multiply-saturated liquid geothermometry. Helz and Thornber (1987) and Grove and Juster (1989) have shown that liquid composition can be used as a purely empirical geothermometer, so long as appropriate restrictions are made on bulk composition and saturating phases. We have calibrated a similar empirical geothermometer for liquids containing plagioclase and at least one Ca-rich ferromagnesian silicate (hornblende or pyroxene), but no low-Ca pyroxene, at pressures of 1 atm to 12 kb. Most calibrating experiments also contain olivine. Calibration points are 35 hydrous and 61 dry experiments. Hydrous data include experiments reported in Table 4 and by Sisson and Grove (1992) and are supplemented by seven additional unpublished experiments at 1-kb H₂O-saturated on an HAB and a BA performed by T.P. Wagner and R. Powers, at the Massachusetts Institute of Technology (Wagner and Powers, written communication 1991). Constraints from hydrous simple systems are the forsterite-diopside-anorthite-H₂O piercing point

at 2 kb (Sisson and Grove 1992) and the diopside-anorthite-H₂O piercing point at 5 kb (Yoder 1965).

Dry liquids have been restricted to non-alkalic compositions that coexist with plagioclase, olivine, and a high-Ca pyroxene but no low-Ca pyroxene (in keeping with the wet experiments). This restriction has the effect of excluding most dry liquids with SiO₂ > 55 wt.%; we recommend that the geothermometer not be used for more silica-rich compositions. Data sources are all of the experiments reported in Grove et al. (1982), Grove and Bryan (1983), Grove et al. (1990), Kinzler and Grove (1985), Tormey et al. (1987), Walker et al. (1979), and Baker and Eggler (1983, 1987) that contain the assemblage olivine-high-Ca pyroxene-plagioclase-liquid but no low-Ca pyroxene at 1-atm. Elevated pressure experiments from Bartels et al. (1991), Kinzler and Grove (1992), and Grove et al. (1992) were used to obtain the pressure dependence of the boundary. Dry simple system constraints are provided by the 1-atm forsterite-diopside-anorthite and diopside-albite piercing points as reported by Presnall et al. (1978) and Schairer and Morimoto (1959) (corrected to IPTS 1968) and two successively lower temperature forsterite-diopside-anorthite saturated melts reported by Presnall et al. (1978).

An empirical model relating liquid composition and temperature uses pressure and four liquid compositional parameters: molar Mg/(Mg + Fe) referred to as Mg[#], wt. % (Na₂O + K₂O)/(Na₂O + K₂O + CaO) referred to as NaK[#], wt. % Al₂O₃/(SiO₂ + Al₂O₃) referred to as Al[#], and wt. % H₂O. These four parameters were found, after extensive testing of alternatives, to yield predicted temperatures that closely approach the temperatures of the 96 experiments used for calibration. The thermodynamic variance in these natural systems is high. If the number of components is assumed to be nine (this includes the dominant major and minor oxides and H₂O), and the number of phases is four (liquid, olivine, plagioclase, high-Ca pyroxene or liquid, olivine, plagioclase, hornblende), the variance of the system is seven. Thus, we must fix pressure and six compositional parameters in order to rigorously constrain temperature (four for those experiments or magmas also saturated with a spinel phase and a fluid or vapor). Our chosen empirical method provides a satisfactory description of the multiple phase saturation between predicted and observed temperatures and in the interest of simplicity only the four most significant terms have been retained. Figure 8 shows the temperature recovery of the model:

$$T^{\circ}\text{C} = 969 - 33.1 * \text{H}_2\text{O} + 0.0052 * (\text{P} - 1) + 742.7 * \text{Al}^{\#} - 138 * \text{NaK}^{\#} + 125.3 * \text{Mg}^{\#}$$

with P in bar. The r^2 for this fit is 0.994, and the expression recovers temperature with an average error of 7 °C for the wet and the dry data.

This liquid geothermometer is surprisingly successful in recovering the temperatures of a large number (96) of calibrating experiments encompassing simple systems, MORBs, and arc basalts at low-to-moderate pressure. The uncertainties in calculated temperatures approach the accuracy of measured experimental temperatures. This geothermometer is simply a numerical description of the variation in temperature across that portion of temper-

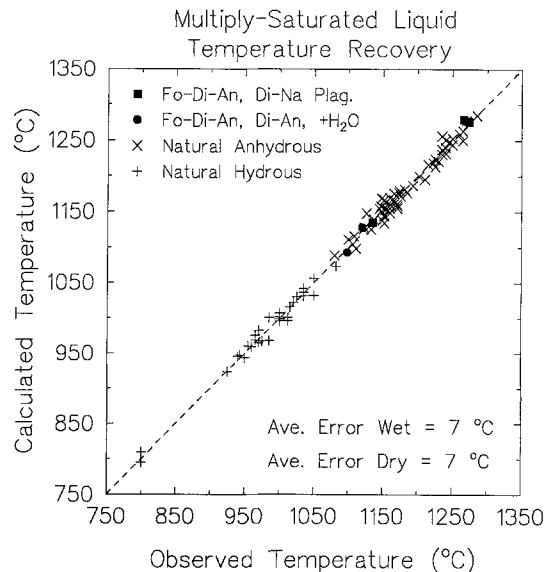


Fig. 8. Observed versus calculated temperatures for experiments that calibrate the multiply-saturated liquid geothermometer. Line represents a 1:1 correspondence

ature-composition space in which common basalts crystallize plagioclase, high-Ca pyroxene or hornblende, with and without olivine. Its chief value is that it provides a sensitive estimate of the interdependence of T and H₂O content for multiply-saturated liquids using simple compositional variables.

The effect of other phases has been tested by applying the geothermometer to hypersthene or pigeonite-bearing liquids from Grove and Juster (1989). Calculated temperatures are low by 15–35 °C indicating that crystallization of low-Ca pyroxene drives liquids to regions of temperature-composition space outside of the calibration of the geothermometer. The empirical liquid geothermometer of Grove and Juster (1989) is preferred for melts known to be saturated in a low-Ca pyroxene.

The linear form of the H₂O term merits comment. More complex expressions were formulated involving speciation of dissolved H₂O into hydroxyl groups and molecular H₂O, but these produced no improvement over the linear expression given. Burnham (1979, his Fig. 6) shows that, at a given pressure, the melting point depression of albite is close to linear with respect to dissolved H₂O for mol fractions of H₂O up to 0.5 (equal to 6.4 wt. %). Silver and Stolper (1984) presented calculated isobaric T-H₂O sections for the system albite-H₂O. Their results also show near-linear melting point depression of albite with added H₂O. These results suggest that a linear expression is a good first approximation for melting point depression effect of H₂O in natural magmas.

Olivine-liquid. The distribution of MgO between olivine and liquid can be used to calculate temperature (Roeder and Emslie 1970; Roeder 1974; Longhi et al. 1978; Ford et al. 1983). We follow the formulation of Longhi et al. (1978) and express K^{Mg} as:

$$K^{\text{Mg}} = (X^{\text{Mg}_{\text{ol}}}) / ((X^{\text{Mg}_{\text{L}}})(X^{\text{Si}_{\text{L}}})^{0.5}),$$

where $X^{\text{Mg}_{\text{ol}}}$ is the mol fraction of MgO in the olivine, and $X^{\text{Mg}_{\text{L}}}$ and $X^{\text{Si}_{\text{L}}}$ are mol fractions of MgO and SiO₂ in

the liquid (modified component choice after Bottinga and Weill 1972, see later). A thermodynamically-based expression relating temperature to K^{Mg} can be of the form:

$$\log(K^{Mg}) = a*(1/T \text{ K}) + b + c*(P - 1)/(T \text{ K}).$$

The coefficients a and c and constant b are calibrated by multiple regression of experimental data.

We use the experimental compositions reported in Table 4 and Sisson and Grove (1992), seven additional experiments on HABs at 1 kb H_2O -saturated, plus anhydrous experiments with coexisting plagioclase-olivine-liquid over the pressure range 1 atm to 12 kb reported in the literature, with preference for compositions also containing a high-Ca pyroxene, but excluding all results with low-Ca pyroxene. Data sources are as noted but were supplemented with 1-atm olivine plus plagioclase-saturated liquids from Grove et al. (1982) and Bartels et al. (1991).

The choice of liquid components directly influences K^{Mg} . The most successful simple formulation used single cation oxide components (ie. MgO , $PO_{2.5}$, $HO_{0.5}$, etc.) with the exception of alumina. Alumina was distributed with all of the alkalis as alkali aluminates, $NaAlO_2$ and $KAlO_2$. The remaining alumina was combined with CaO as $CaAl_2O_4$. This choice of components was found to remove much of the effect of variable alkali content on K^{Mg} noted in previous studies (Roeder 1974; Longhi et al. 1978).

The coefficient and constant terms a , b , and c were determined by multiple regression of $\log(K^{Mg})$ against $1/(T \text{ K})$ and $(P-1)/(T \text{ K})$. Data points lying outside of the 2σ uncertainty of the regression were excluded (1140Mf no. 18, A-3 of Kinzler and Grove 1985, and ALV2-9 of Grove et al. 1992), and the regression was repeated. The final calibrating data set consists of 36 wet and 66 dry experiments giving:

$$\log_{10}(K^{Mg}) = 4129*(1/T \text{ K}) - 2.082 + 0.0146*(P - 1)/(T \text{ K})$$

The correlation coefficient (r^2) for the regression is 0.985 and the expression recovers temperature for wet and dry experiments used for calibration with an average error of 8°C and 11°C respectively (Fig. 9). Residuals (observed-expected) show statistically significant correlations with liquid FeO and TiO_2 contents. Predicted temperatures for melts with $FeO \geq 13.5 \text{ wt.}\%$ and $TiO_2 \geq 3.5 \text{ wt.}\%$ (eg., evolved tholeiites) are up to 30°C higher than their true temperatures, likely due to shortcomings in the melt solution model. We recommend that use of this olivine-liquid geothermometer be restricted to magmas with $SiO_2 \leq 55 \text{ wt.}\%$, $FeO \leq 13 \text{ wt.}\%$, and $TiO_2 < 3 \text{ wt.}\%$. *Plagioclase-liquid.* Housh and Luhr (1991) used the distribution of albite and anorthite components between plagioclase and melt to model the effects of H_2O on the mineral-melt equilibria. The data used to calibrate their model include no H_2O -bearing basaltic liquids ($SiO_2 \leq 52 \text{ wt.}\%$, for analyses normalized to 100% volatile-free). We have applied their formulation to the hydrous experiments reported in Sisson and Grove (1992) and Table 4, and find that the anorthite-melt expression recovers melt H_2O contents (calculated by Burnham's method) with an average error of 0.35 wt.%. The anorthite-melt formulation of Housh and Luhr (1991) is used here

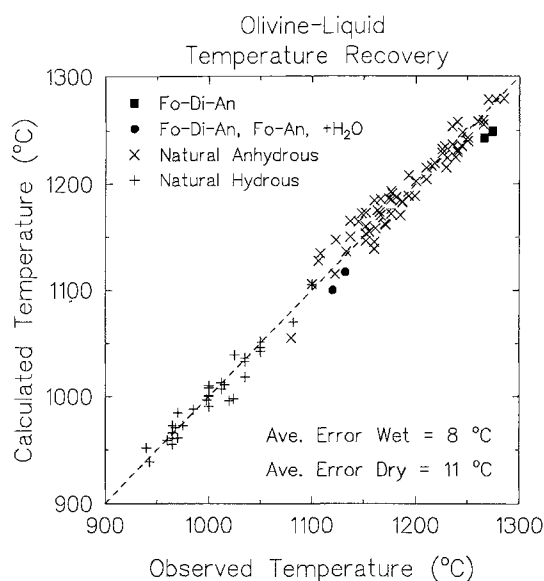


Fig. 9. Observed versus calculated temperatures for experiments that calibrate the olivine-liquid geothermometer. Line represents a 1:1 correspondence

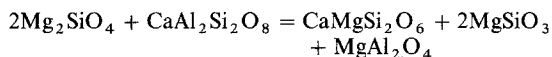
as an additional constraint for estimating the H_2O contents of common HABs. The albite-melt expression of Housh and Luhr (1991) consistently overestimates the H_2O contents of 1 and 2 kb experimental liquids by as much as 2.7 wt.% and is not considered further.

Three constraining expressions are used later to estimate the temperature and H_2O content of magmas that contain the appropriate phase assemblage. In principle, the three expressions could be solved simultaneously to obtain a unique solution for temperature, pressure, and H_2O content. However, the plagioclase-melt geothermometer of Housh and Luhr (1991) only incorporates pressure in calculating the influence of the orthoclase component of plagioclase on the activities of anorthite and albite. For the very K-poor plagioclase of HABs, the plagioclase-melt geothermometer effectively ignores pressure. Accordingly, we refrain from simultaneous solution to obtain pressure, temperature, and H_2O content; instead we specify pressure and compute T and H_2O content.

Quantitative estimates of the temperatures and H_2O contents of high-alumina basalts and basaltic andesites

Given a pressure estimate and assuming that HABs and BAs were multiply-saturated liquids, the olivine-liquid and multiply-saturated liquid geothermometers can be used to estimate T and H_2O content. The bulk liquid geothermometer yields a temperature directly. The olivine-liquid geothermometer requires an equilibrium olivine composition, but this can be estimated using the olivine-liquid Fe-Mg exchange K_D (0.29). The most calcic plagioclase core composition is used for the liquidus plagioclase in the anorthite-liquid expression of Housh and Luhr (1991) to provide additional estimates of T and wt.% H_2O by simultaneous solution with the olivine-liquid or bulk liquid expressions.

A lower limit to the pressure of equilibration is that required to hold the estimated H₂O content in solution in the melt. An approximate upper pressure is provided by the coexistence of magnesian olivine and calcic plagioclase and the reaction:



For typical low-MgO HAB (0.5 = Mg/Mg + Fe) we use plagioclase of An₉₂, Cr-Al-Mg spinel from Sisson and Grove (1992), and other phase compositions from mineral-melt exchange $K_D^{\text{Fe-MgS}}$: oliv = 0.29, cpx_(Di-Hd) = 0.22, opx_(En-Fs) = 0.18. Activities are estimated as $a_{\text{An}} = X_{\text{An}}$, a_{spinel} by the formulation of Sack (1982), and other phases by ideal mixing on sites. Pressures calculated with the thermochemical data of Ghiorso et al. (1983; Tables A2-1, A2-2) lie in the range 6.5–8 kb for temperatures from 1000°C–1100°C. Either olivine or calcic-plagioclase would be absent at higher pressures. Lower pressures are obtained if the high-Ca pyroxene is assumed to contain an En-Fs component and the low-Ca pyroxene a Di-Hd component. We conclude that it is unlikely that the calcic-plagioclase and olivine in low-MgO HABs formed at pressures significantly higher than 8 kb.

Three tests are made of the temperature and H₂O contents using olivine-liquid and multiply-saturated liquid geothermometers.

(1) Muenow et al. (1990) provide analyses of volatiles (including H₂O) and major elements in three fresh basalt and basaltic andesite glasses quenched at seafloor pressures in the Troodos ophiolite. One glass contains microphenocrysts of olivine, high-Ca pyroxene, and plagioclase (Rautenschlein et al. 1985). Petrographic descriptions are not available for the other samples. The measured H₂O contents are 2.11, 2.30, and 2.12 wt.%. H₂O contents calculated with the two geothermometers for a pressure of 500 bar are 3.0, 3.0, and 2.6 wt.% respectively, in acceptable agreement with the measured values.

(2) Garcia et al. (1989) measured the H₂O contents of Hawaiian basalt glasses quenched at seafloor depths of about 2 km. Thirteen of the 39 analyzed glasses contain the phenocryst assemblage olivine-high-Ca-pyroxene plagioclase and therefore are appropriate for the multiply-saturated liquid and olivine-liquid geothermometers. These thirteen glasses have an average H₂O content of 0.40 ± 0.20 wt.%. The average H₂O content calculated for the same glasses for a pressure of 200 bar is 0.68 ± 0.39 wt.%.

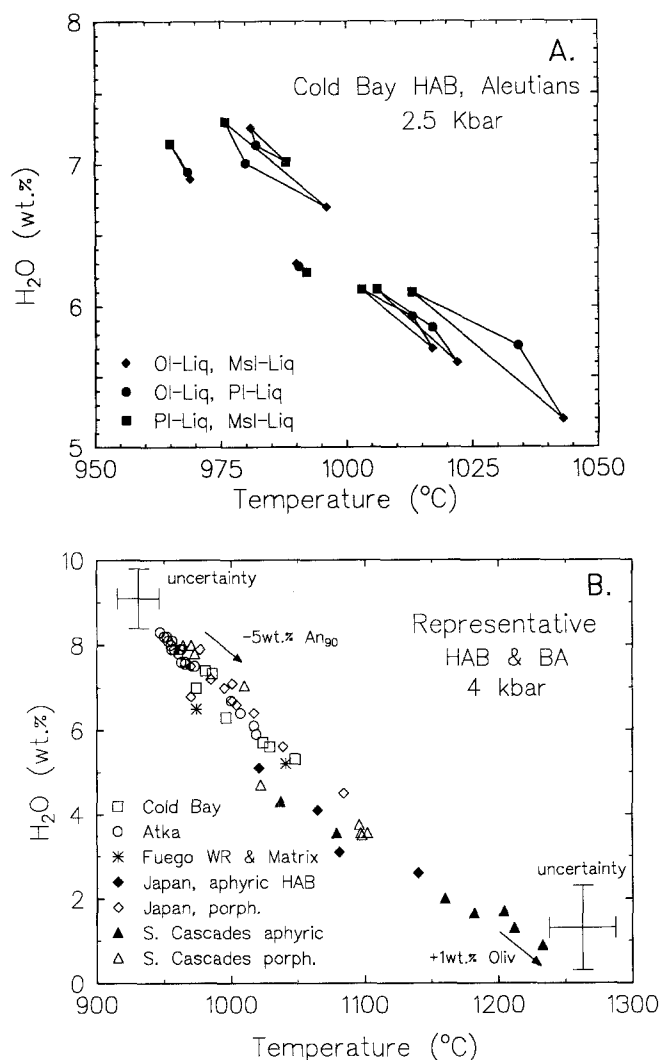
The experiments of Baker and Eggler (1983) on a HAB from the volcanic center at Atka in the Aleutians provide the third test of the technique. Baker and Eggler (1983) show that Akta rock AT-1 exists as a multiply-saturated liquid near 1000°C, at 2 kb, with dissolved H₂O between 4 and 6 wt.%. Our calculations for 2 kb predict AT-1 would exist as a multiply-saturated liquid at 1009°C with 6.0 wt.% dissolved H₂O. The results of these tests show that the H₂O estimation technique allows us to distinguish between basaltic melts with low (< 2 wt.%), moderate (2–4 wt.%), and high (> 4 wt.%) H₂O contents so long as those melts meet the constraints of appropriate phase assemblage. We emphasize later that in

applications to rocks the technique is no more accurate than this.

The estimation technique is applied first to the low-MgO HABs of the Cold Bay volcanic center of the Aleutians that were discussed already assuming that the lavas were multiply-saturated liquids at pressure of 2.5 kb (Fig. 10a). Plagioclase core compositions for Cold Bay rocks reported by Brophy (1986) allow for two additional estimates of temperature and H₂O through the anorthite-liquid model of Housh and Luhr (1991). The three estimates of temperature and H₂O content are in good agreement (Fig. 10a) and support the arguments presented above that Aleutian low-MgO HABs are H₂O-rich and comparatively low temperature magmas that were once multiply-saturated liquids. For higher pressures, temperatures and H₂O contents estimated from the combined olivine-liquid and multiply-saturated liquid geothermometers increase by about 4°C and about 0.036 wt.% H₂O/kb. At 8 kb temperatures and H₂O contents would be about 22°C and about 0.2 wt.% higher than those shown in Fig. 10a. The high H₂O contents rule out equilibration pressures significantly lower than 2.5 kb.

Singer et al. (1992) present whole-rock and phenocryst analyses for HABs and related lavas from the Seguam volcanic center in the Aleutians and argue that the Seguam lavas preserve a liquid line of descent. Seguam HAB J87-79 contains magnetite and ilmenite that provide an independent estimate of magmatic temperature. Assuming uncertainties of ± 0.01 in the mol fractions of ulvospinel and ilmenite, the oxide analyses give an equilibration temperature in the range 1040°C–1100°C or 1082°C for the analyses as reported (Singer et al. 1992). Temperatures and H₂O contents calculated assuming that J87-79 was an appropriately saturated liquid range from 1047°C and 5.6 wt.% at 2 kb to 1071°C and 5.8 wt.% at 8 kb. Plagioclase phenocryst cores in J87-79 reach An₉₆. Assuming again that the whole-rock was a liquid, the plagioclase-melt expression gives 6.0 wt.% H₂O at 1040°C and 5.0 wt.% at 1100°C. If the Seguam HABs were multiply-saturated liquids at crustal pressures, as argued by Singer et al. (1992), our estimates show that the liquids contained more than 4 wt.% H₂O and were no hotter than 1100°C.

Figure 10b shows calculated temperatures and H₂O contents for a suite of representative HABs and BAs, with results obtained with the olivine-liquid and multiply-saturated liquid geothermometers. These are the temperatures and H₂O contents at which the rocks would have been liquids if they were multiply-saturated at a pressure of 4 kb. This pressure was assumed simply because it would allow the H₂O content calculated for most samples to remain in solution. As with the Cold Bay and Seguam samples, different assumed pressures lead to small changes in estimated H₂O and temperature. Samples range from aphyric MgO-rich HAB from the southern Cascades of California to strongly plagioclase-porphyrific low-MgO HAB and BA from the Aleutians. Including the ground-mass composition for the 1974 eruption of Fuego, aphyric material records temperatures from about 1230°C down to 975°C and H₂O contents from 1 to 6.5 wt.%. On the whole, porphyritic samples record lower temperatures and higher H₂O contents compared with the aphyric rocks. Figure 10b shows that if the porphyritic HABs



were multiply-saturated liquids then they existed at temperatures far lower than are commonly proposed for basaltic magma. Figure 10b also shows that to exist as multiply-saturated liquids, the porphyritic samples would require H₂O contents generally in excess of 4 wt.%, consistent with the arguments presented already.

Some of the aphyric magnesian HABs of the southern Cascades plotted in Fig. 10b probably have crystallized small amounts of olivine or olivine and plagioclase at shallow levels and no longer preserve the compositions of multiply-saturated liquids at base-of-crust pressures (Bartels et al. 1991). Phenocryst assemblages are traces of plagioclase and olivine but lacking high-Ca pyroxene (Gerlach and Grove 1982). Fractionation of olivine alone depletes the melt in MgO and leads to overestimates of the H₂O content. For example, sample 79-35 g (Table 1) yields a temperature of 1212°C and 1.3 wt.% H₂O at 4 kb. Addition of 1 wt.% equilibrium olivine changes the estimates to 1245°C and 0.3 wt.% H₂O. Estimates for samples with lower MgO and lower Mg number are less sensitive. The average HAB from the Cold Bay center, Aleutians (Table 1) gives 1023°C and 5.9 wt.% H₂O at 4 kb and addition of 5 wt.% equilibrium olivine changes the estimates to 1084°C and 4.1 wt.% H₂O. As shown

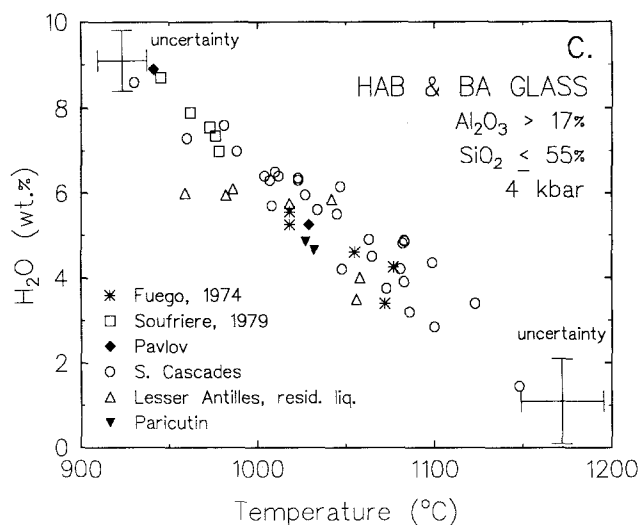


Fig. 10. **A** Temperature and wt.% H₂O calculated for HABs from the Cold Bay volcanic center, Aleutians, at 2.5 kb pressure (analyses from Brophy 1986). *Diamonds*, olivine-liquid and multiply-saturated liquid solutions; *dots*, olivine-liquid and plagioclase-liquid solutions; *squares*, plagioclase-liquid and multiply-saturated liquid solutions. *Lines* connect solutions for each sample. Calculations assume: whole-rocks preserve liquid compositions, the most calcic measured plagioclase is the liquidus composition, olivine-melt $K_D^{Fe-Mg} = 0.29$ with all Fe as FeO. **B** Temperature and wt.% H₂O for representative HABs and BAs. Temperatures and H₂O contents are calculated by simultaneous solution of olivine-liquid and multiply-saturated liquid geothermometers at 4 kb pressure, olivine-melt $K_D^{Fe-Mg} = 0.29$ with all Fe as FeO. Uncertainties assume errors in the olivine-liquid geothermometer of $\pm 12^\circ\text{C}$ at low melt H₂O and $\pm 8^\circ\text{C}$ at high melt H₂O and error for the multiply-saturated liquid geothermometer of $\pm 7^\circ\text{C}$. *Upper arrow* shows the effect of subtracting 5 wt.% An₉₀ plagioclase from a typical HAB from Cold Bay, Aleutians and then calculating temperature and H₂O content. *Lower arrow* shows the effect of adding 1 wt.% equilibrium olivine to a high-MgO HAB and then calculating temperature and H₂O content. Data from Brophy (1986), Myers et al. (1986), Kuno (1950, 1960), Rose et al. (1978), Gerlach and Grove (1982), and unpublished data of T.L. Grove and J. Donnelly-Nolan. **C** Temperature and wt.% H₂O for HAB and BA glass inclusions and residual quenched liquids in cumulate xenoliths. Calculations and uncertainties as in **B**. Data from Anderson (1973, 1974a, b, 1979, 1982), Rose et al. (1978), Arculus and Wills (1980), Devine and Sigurdsson (1983), and Harris and Anderson (1984)

already the H₂O and temperature estimates are accurate for multiply-saturated melts. Application to rocks requires caution and is best made in conjunction with other geothermometric and hydrometric techniques as illustrated above for samples from Cold Bay and Seguan.

Figure 10c shows calculated temperatures and H₂O contents for natural HAB and BA liquids, with results obtained with the multiply-saturated liquid and olivine-liquid geothermometers at 4 kb. The samples are both inclusions of glass in olivine phenocrysts and interstitial glass and scoria from erupted cumulate nodules. Most compositions are near the transition between basalt and basaltic andesite (SiO₂ = 52 \pm 1 wt.%), have Al₂O₃ in the range 18–20 wt.%, and MgO = 4 \pm 1 wt.%, and thus are similar to porphyritic HABs and BAs. MgO ranges as high as 7.6 wt.% and as low as 1.8 wt.%. The calculated temperatures and H₂O contents for the natural liquids

cover much the same range as the erupted HAB and BA lavas and scoria. MgO in glasses does not reach as high as in the rocks and the upper temperature is accordingly lower than for the rocks. Figure 10c shows that greater than 90% of the natural HAB and BA liquids preserved as glass and intercumulus groundmass had H₂O contents higher than 3 wt.% and were cooler than 1100°C.

The plagioclase accumulation hypothesis

Crawford et al. (1987) propose that porphyritic, low-MgO HABs never exist as liquids and form instead by the accumulation of plagioclase phenocrysts in liquids with lower alumina. Modest accumulation of phenocrysts certainly occurs and has been carefully documented in some cases (Rose et al. 1978). We question, however, whether accumulation of plagioclase is responsible for the major characteristics of low-MgO HABs and BAs. The abundance of these magmas in arcs and their scarcity elsewhere (Kuno 1960) suggests that a special feature of arc magmatism is responsible for their high-alumina and low-MgO. There is a well-defined upper limit to the alumina content of porphyritic HABs. Volcanic rocks with Al₂O₃ ≥ 20 wt.% are rare and volcanic rocks with > 21 wt.% Al₂O₃ are very uncommon. Aphyric HABs with Al₂O₃ approximately 18 wt.% are present at some arc volcanic centers (Kuno 1960; Gerlach and Grove 1982) and plagioclase accumulation in these would produce a gradation to very high alumina. Accumulation of 30 wt.% An₉₀ plagioclase (typical of the amount and type of phenocrysts found) into liquid with 18 wt.% Al₂O₃ would yield magma with 23 wt.% Al₂O₃, considerably in excess of observed Al₂O₃ contents. In contrast, the upper limit to alumina contents finds ready explanation as the maximum solubility of Al₂O₃ in hydrous basaltic liquid saturated in plagioclase, olivine, and either high-Ca pyroxene or hornblende at crustal pressures.

Melting in the mantle wedge

Several experimental studies have shown that HABs with high-MgO (≥ 8.5 wt.%) can be produced by anhydrous melting of plagioclase or spinel ilmenite near 10 kb pressure (Fujii and Scarfe 1985; Takahashi 1986; Falloon and Green 1987; Bartels et al. 1991). The dry liquids do not crystallize to low-MgO HABs and cannot produce the mineral compositions found in low-MgO HABs. Our results support the proposal that low-MgO HABs are fractionated hydrous liquids that have partly degassed and crystallized prior to eruption and that their parental primary magmas have 2.5–4.5 wt.% H₂O. Apparently, some primary arc magmas are (nearly) dry whereas others contain as much as several wt.% H₂O. H₂O must be inhomogeneously distributed in the mantle wedge with some parts of the mantle wedge nearly dry and capable of melting to form high-MgO HABs. Other areas either contain hydrous minerals or a free volatile phase in sufficient abundance that derived melts contain as much as a few wt.% H₂O.

Conclusion

H₂O is a major constituent of some of the most common basalts erupted in arcs. Low-MgO HABs are explicable as liquids saturated with their observed phenocrysts at crustal pressures so long as the melts have 4 or more wt.% H₂O. At these conditions the melts are saturated with olivine as well as other minerals and thus low-MgO HABs could originate by simple crystallization differentiation of mantle-derived hydrous primary basalts. Wet low-MgO HABs cannot normally erupt as liquids. They must degas at shallow depths and this will force them to grow phenocrysts. Their abundant phenocrysts probably crystallize within the mid-to-upper crust as the magma ascends and decompresses and the liquid dehydrates.

Further experimentation is required to establish the relation of evolved wet HABs to potential primary magmas. Nevertheless, our results support models in which H₂O carried and released by the subducting slab fluxes the mantle and initiates melting (McBirney 1969; Nicholls and Ringwood 1973; Ringwood 1975; Tatsumi et al. 1983). The eruption of magnesian HABs with low H₂O shows that H₂O is inhomogeneously distributed in the sub-arc mantle and therefore the degree to which subducted and recycled H₂O is essential for the creation of arc magmas remains to be determined.

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