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AMPHIBOLE STABILITY IN H_2O-UNDERSATURATED CALC-ALKALINE MELTS

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The upper stability limit of amphibole in silicate melts has previously been shown to increase in temperature when the mole fraction of H_2O in the fluid phase in equilibrium with the melt was decreased from 1.0 to 0.5. New experiments on amphibole stability in melts of andesite composition show that the amphibole stability limit also decreases in temperature when mole fraction H_2O in fluid is less than 0.5; these experiments imply that there is an isobaric temperature maximum of stability. At 5.5 kb this maximum occurs at a melt composition of 4.5 percent H_2O for andesite composition. The maximum at 5.5 kb may be explained by a change in amphibole breakdown from an incongruent melting reaction to a dehydration reaction. Calculations in the pressure range 0–10 kb indicate that the isobaric temperature maximum of amphibole stability occurs at a mole fraction of H_2O in the fluid phase ranging from 1.0 to 0.4, depending on total pressure. The maximum may represent either a melting or a dehydration reaction. Calculations also suggest that above 8 kb amphibole is as stable in silicate melt when the mole fraction of H_2O in the fluid phase is 0.3 as when the mole fraction is 1.0. Such conditions affirm the possibility of hydrous partial melting of amphibole-bearing basalt in the earth's mantle to form the calc-alkaline series.

1. Introduction

In recent years increasing attention has been paid to the roles of H_2O and of H_2O-bearing minerals in the earth's lower crust and upper mantle, especially with regard to the generation of basaltic and calc-alkaline magmas. Several recent studies have investigated the stability of hydrous minerals in silicate liquids undersaturated with H_2O [1–3]. These studies have demonstrated that the upper temperature stability limit of hydrous phases in H_2O-undersaturated melts may be higher than their stability limit in H_2O-saturated melts. New experiments on melting relations in andesite include runs which demonstrate that the upper stability limit of amphibole may either increase or decrease in temperature over a range of degrees of H_2O-undersaturation.

2. Definitions

In this paper H_2O-saturation refers to a system in which the fugacity of H_2O in a melt phase ($f^{m}_{H_2O}$) equals $f^{o}_{H_2O}$, the fugacity of pure H_2O at the same temperature and total pressure. Strictly speaking, every system therefore is H_2O-undersaturated ($f^{m}_{H_2O}$ less than $f^{o}_{H_2O}$), because a small amount of solids dissolves in the fluid. However, in thermodynamic calculations these solids are ignored, and although 'H_2O-saturation' may be theoretically impossible, its meaning is clear. In experiments described herein, a fluid phase of $H_2O + CO_2$ is always present, such that $f^{m}_{H_2O}$ equals H_2O fugacity in the fluid phase, $f^{fl}_{H_2O}$. This paper assumes ideal mixing of H_2O in that fluid ($f^{fl}_{H_2O} = f^{o}_{H_2O} \times X^{fl}_{H_2O}$). Standard states of phases as defined here are consistent with standard state set B of Anderson [4], whose method was used for dehydration calculations.

3. Experimental techniques

Runs were made in Pd-Ag capsules in an internally-heated pressure vessel from 2 to 8 kb and in a piston-cylinder apparatus at 10 kb. Undersaturation of the melt was achieved by adding oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) to the sample capsule. In the sealed capsule at experimental conditions equal molar amounts of CO_2 and H_2O are initially produced [5]. However, because CO_2 is insoluble in the melt [6], while H_2O is soluble, CO_2 enters the fluid phase entirely, and H_2O is partitioned between fluid and melt. The $X^{fl}_{H_2O}$ is therefore less than 0.5, and, correspondingly, $f^{fl}_{H_2O}$ ($= f^{m}_{H_2O}$) decreases. By this procedure, the solubility of H_2O in the melt may be controlled, because H_2O solubility is a function of pressure, temperature, and $f^{m}_{H_2O}$ [7]. H_2O fugacity may be calculated from thermodynamic data [7] and the mode of a run. Experimental details will be discussed elsewhere [8]. Oxygen fugacity was controlled by fixing P_{H_2} with a hydrogen membrane [9] to give a f_{O_2}, calculated from the $f^{m}_{H_2O}$, equal to that of the QFM buffer for the temperature and total pressure of the run.

Runs were made on andesite FP-16-52 from Paricutin Volcano, Mexico. Analyses of the andesite and of two experimentally-produced amphiboles are given in table 1. A few runs were made on a sample of 1921 Kilauea tholeiite, described in [3].

4. Results

Melting relations for the Paricutin andesite under H_2O-saturated conditions (summarized in fig. 1) have been previously described [8]. Amphibole in this rock composition is a near-liquidus phase only above 6 kb under H_2O-saturated conditions. Its stability has been closely examined at 5.5 kb in both H_2O-saturated and undersaturated runs (fig. 2). Although the upper stability limit of amphibole at H_2O-saturated conditions was determined precisely only at 2 kb, its amphibole-out temperature can be drawn with some confidence because at 2 kb this amphibole breaks down at 930 ± 5°, precisely the same as in a Mt. Hood andesite, which has a well-determined H_2O-saturated amphibole-out curve [10, 11].

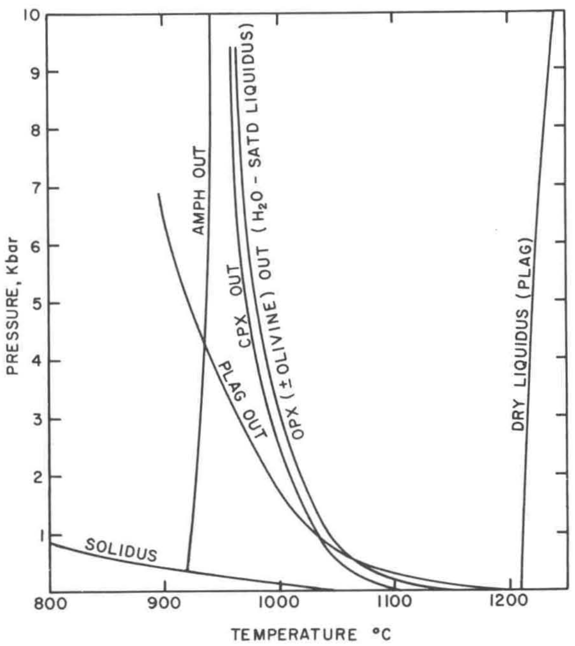

Fig. 1. Melting relations in Paricutin andesite FP-16-52. Curves refer to H_2O-saturated conditions, except for the dry liquidus at right.

Table 1
Analyses of Paricutin andesite (FP-16-52) used in study and of two amphiboles from experimental runs. All analyses by electron microprobe; rock analysis on a hydrothermal run held above liquidus, calculated H_2O-free.

	FP-16-52	Amph.	Amph.
Temp (°C)		930	900
Pressure (kb)		5.8	5.5
Wt % H_2O in melt		4.7	10.3
SiO_2	60.5	40.7	45.0
TiO_2	0.91	2.94	1.61
Al_2O_3	17.3	12.9	9.6
FeO	4.3	13.6	10.3
MgO	3.8	13.1	16.1
CaO	6.3	10.8	11.7
Na_2O	4.3	2.58	2.46
K_2O	1.69	0.57	0.54
	99.10	97.19	97.31

In fig. 2 runs to delimit amphibole stability have been labeled with that weight percent H_2O which was calculated to be present in melt of the run. At 5–6 kb runs with 10–11 percent H_2O in melt represent H_2O-saturated conditions; runs containing 4.7 percent H_2O had $X^{fl}_{H_2O}$ = 0.~~43~~ .50. The runs containing 4.7 percent H_2O indicate that lowering $X^{fl}_{H_2O}$ from 1.0 to 0.5 changed the upper stability limit of amphibole very little up to 6 kb. The amphibole-out curve for $X^{fl}_{H_2O}$ = 0.5 probably lies near or up to 15° above the H_2O-saturated amphibole-out curve at 5.5 kb. This condition agrees with results from basalt composition experiments (see below). However, when $X^{fl}_{H_2O}$ was

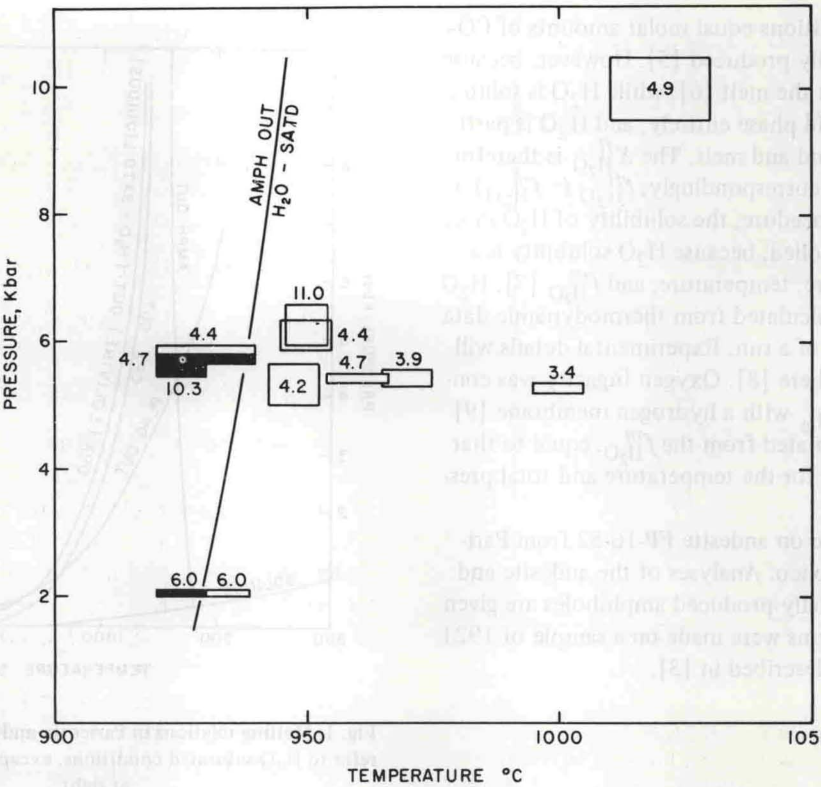

Fig. 2. Results of runs on amphibole stability in Paricutin andesite. Solid brackets indicate amphibole present; open brackets indicate amphibole absent. Size of brackets represents estimated errors in measured pressure and temperature. Numbers are weight percent H_2O in melt.

lowered from 0.5 to 0.43 (weight percent H_2O in melt lowered from 4.7 to 4.4), the upper stability limit of amphibole was *lowered*. Two runs at 5.8 kb, 930°C clearly show this effect, because for 4.7 percent H_2O the limit must lie above, and for 4.4 percent H_2O below, 930°. These capsules were run side-by-side at exactly the same experimental conditions, except for amount of oxalic acid added to the capsule. It is anticipated that further lowering of $X^{fl}_{H_2O}$ would further decrease amphibole stability. Unfortunately, experimentation in the lower temperature-lower water content range is difficult because of problems in attaining equilibrium, in determining percent glass of the run, and in having confidence in the ideal mixing assumption for H_2O–CO_2 fluids.

These results on andesite may be compared to experiments on basalt. Hill and Boettcher [12] demonstrated that above 13 kb the upper stability of amphibole in 1921 Kilauea tholeiite was raised 50–120°C when $X^{fl}_{H_2O}$ was decreased from 1.0 to 0.5. New experiments on 1921 tholeiite at 2 kb, when combined with data of Holloway and Burnham (fig. 3), indicate that at low pressure the change in stability limit is much less, 0–15°C.

Basalt differs from andesite in that amphibole stability is about 60°C higher, and more modal amphibole is present in basalt runs, because of the greater normative amphibole content of basalt. However, amphibole compositions are similar in runs of both compositions.

5. Discussion

Holloway [3] suggested the instability of amphibole in 1921 tholeiite at 5 kb was a melting reaction:

$$100 \text{ amph} = 23 \text{ cpx} + 77 \text{ liquid} \qquad (1)$$

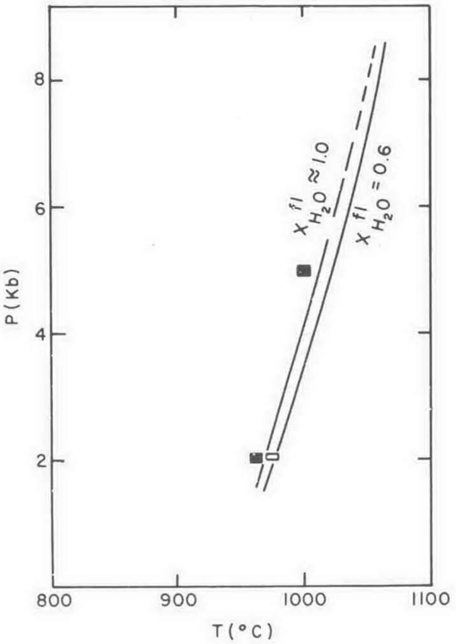

Fig. 3. Amphibole stability in 1921 Kilauea tholeiite. Curve for $X^{fl}_{H_2O} = 0.6$ from Holloway [3]. Brackets, with representations as in fig. 2, refer to H_2O-saturated runs at QFM buffer. Run at 5 kb by R. Tuthill (reported in [3]).

The reaction is written in weight percent. Recognizing that the H_2O-undersaturated liquid contains 4.7 percent H_2O at 5.0 kb, and that amphibole contains 2 percent H_2O, we may rewrite the reaction:

$$100 \text{ amph} + 1.6\ H_2O = 23 \text{ cpx} + 77 \text{ liquid} \tag{2}$$

This equation predicts the increased stability of amphibole with decreased f_{H_2O}. However, experiments explained above show that as weight H_2O in melt is decreased below 4.5 percent at 5.5 kb, amphibole stability decreases, and that an isobaric maximum of stability exists. Since eq. (2) does not predict this behavior, another equation is needed. Two possibilities are a modification of (2),

$$100 \text{ amph} = x \text{ cpx} + y \text{ liquid} + z\ H_2O \tag{3}$$

and the subsolidus dehydration reaction:

$$\begin{aligned}
&\underset{\text{quartz}}{2.60\ SiO_2} + \underset{\text{amphibole}}{1.0\ Na_{0.74}K_{0.10}Ca_{1.71}(Mg_{2.89}Fe^{2+}_{1.29}Fe^{3+}_{0.40}Ti_{0.33}Al_{0.27})Al_{1.98}Si_{6.02}O_{22}(OH)_2} = \underset{\text{K-feldspar}}{0.11KAlSi_3O_8} +\\
&\underset{\text{in plagioclase}}{0.74NaAlSi_3O_8} + \underset{\text{in plagioclase}}{0.71\ CaAl_2Si_2O_8} + \underset{\text{orthopyroxene}}{2.65\ (Mg,Fe)SiO_3} +\\
&\underset{\text{clinopyroxene}}{1.02\ Ca(Mg,Fe)Si_2O_6} + \underset{\text{opaque oxides}}{0.33\ FeTiO_3 + 0.21\ Fe_3O_4} + 1.0\ H_2O.
\end{aligned} \tag{4}$$

The amphibole composition is that of analysis 2, table 1. At temperatures above the solidus, SiO_2 and $KAlSi_3O_8$ undoubtedly melt just above the solidus; the other breakdown products are solid phases, except plagioclase above 4.5 kb in H_2O-saturated melts.

Reaction (3) is possible if the 2.0 percent H_2O produced by amphibole breakdown is greater than the weight solubility of H_2O in the melt at the total pressure, temperature and $X^{fl}_{H_2O}$ of interest. Such a condition results when H_2O solubility in the melt decreases with decreased $X^{fl}_{H_2O}$ or when the amount of melt is decreased by an increased ratio of x to y. Assuming the coefficients of (3) at 5 kb hold in andesite melt at 5.5 kb, however, so that $x = 23$ and $y = 77$ (weight), a liquid containing 4.4 percent H_2O cannot be produced by melting 100 percent amphibole. It appears that z is negative for andesite melt containing 4.4 percent H_2O at 5.5 kb, and that eq. (3) is invalid.

Eq. (4) remains to explain the observed behavior. Because the solidus temperature approaches the temperature of the amphibole-out curve when $X^{fl}_{H_2O}$ is decreased (fig. 4), this reaction is intuitively reasonable. The calculations of fig. 4 show also that the reaction is thermodynamically reasonable. These calculations are based on the argument that amphibole will melt by reaction (2) only within its stability field, and that the amphibole-out reaction will change from melting to dehydration when the isobaric dehydration curve for any $X^{fl}_{H_2O}$ is lower in temperature than the metastable melting curve for the same $X^{fl}_{H_2O}$ and total pressure. It follows that at those isobaric points at which the reaction changes, the dehydration and melting curves for a particular $X^{fl}_{H_2O}$ must cross, because at those points $f^{m}_{H_2O}$ calculated for the melting reaction is equal to $f^{fl}_{H_2O}$ calculated for the dehydration curve.

By the above reasoning, one point on the family of dehydration curves is known, 935°C at 5.5 kb for $X^{fl}_{H_2O} = 0.44$. Strictly speaking, dehydration at those conditions is not equivalent to dehydration of reaction (4), because SiO_2, $KAlSi_3O_8$, and, for H_2O contents in melt greater than 4.7 percent, the oxide phases are dissolved in the melt. However, only activity of SiO_2 is quantitatively significant in the equilibrium constant, and its activity in Paricutin melt, calculated from compositions of coexisting olivine and orthopyroxene in experimental runs and the thermochemical data of Williams [13], is nearly 1.0. Another point on the family of curves was assumed from the intersection of the H_2O-saturated amphibole-out curve and the solidus. From these two points and the molar volume change of the solid phases for reaction (4), the family of dehydration curves (fig. 4a) was constructed.

In fig. 4b the H_2O-saturated amphibole-out curve is assumed to be the melting reaction of eq. (2). Although the position of this curve for lower $X^{fl}_{H_2O}$ is not known, it must lie to the right of the H_2O-saturated position, as long as the melting reaction is (2), not (3).

Fig. 4c combines the curves of figs. 4a and 4b to produce amphibole-out curves which would be observed experimentally at various $X^{fl}_{H_2O}$. Although the curves are not claimed to be positionally correct quantitatively, their relative schematic position is probably correct. According to fig. 4c, for a $X^{fl}_{H_2O} = 1$, the observed amphibole-out curve is a melting reaction at all pressures above 900 bars, a pressure below which the dehydration curve for $X^{fl}_{H_2O} = 1$ marks the upper stability limit of amphibole. At a $X^{fl}_{H_2O} = 0.2$, the upper stability limit of amphibole is the dehydration reaction at all pressures. Therefore the amphibole melting curve for $X^{fl}_{H_2O} = 0.2$ in fig. 4b is metastable. For $X^{fl}_{H_2O}=$

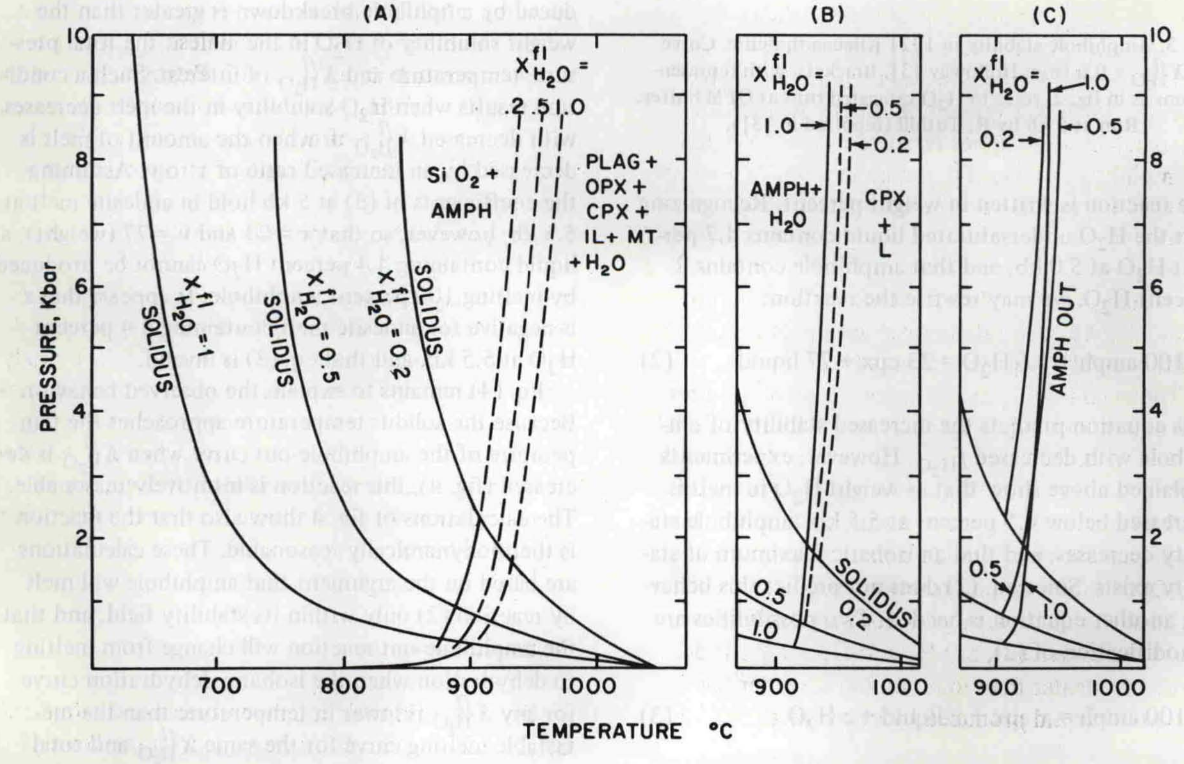

Fig. 4. Schematic *P-T* projection of solidus and amphibole-out reactions for various $X^{fl}_{H_2O}$. (a) Solidus for andesite-H_2O, after tonalite solidus of [14]; H_2O-undersaturated solidi, calculated from data of [15]; and amphibole + quartz dehydration curves, dashed where metastable. (b) Incongruent melting curves of amphibole in andesite melt for $X^{fl}_{H_2O} = 1.0$ (experimental) and 0.2 and 0.5 (dashed, may be metastable). (c) Upper stability limits of amphibole in andesite melt for various $X^{fl}_{H_2O}$.

0.5, the observed amphibole-out curve is a melting reaction above 4.5 kb. Between 3.5 and 4.5 kb, the upper temperature stability of amphibole is limited by the dehydration curve, although that curve lies above the H_2O-saturated amphibole-out curve. Below 3.5 kb, the upper stability limit is still the dehydration curve, but the amphibole-out curve now lies below the H_2O-saturated curve.

Fig. 4c correctly predicts observed melting behavior at 5.5 kb. The amphibole-out curve for $X^{fl}_{H_2O}$ = 0.5 lies above the curve for $X^{fl}_{H_2O}$ = 1. The 0.5 curve also lies near a temperature stability maximum, because when $X^{fl}_{H_2O}$ is less than 0.44, the amphibole-out curve descends in temperature with decreasing $X^{fl}_{H_2O}$.

6. Summary

Experiments and theory developed in this paper indicate that the upper temperature limit of amphibole stability in a melt is a function of pressure, temperature and $f^{m}_{H_2O}$, the fugacity of H_2O in the melt. Moreover, to fully characterize amphibole stability, we must relate those intensive parameters to possible reactions involving amphibole. In calcalkaline melts, it appears that the upper temperature stability limit of amphibole for any $X^{fl}_{H_2O}$ may represent either an incongruent melting or a dehydration reaction, depending upon total pressure and composition of the fluid phase in equilibrium with the melt. The *maximum* upper temperature stability limit may lie either above or below the H_2O-saturated upper temperature stability limit, depending upon total pressure.

The maximum upper temperature stability limit was determined experimentally at 5.5 kb in andesite melt. The temperature is 940°C, at a H_2O content in melt of 4.5 percent ($X^{fl}_{H_2O}$ = 0.44). The maximum at 5.5 kb represents the point at which amphibole breakdown changes from a predominantly melting reaction (eq. 2) to a dehydration reaction (eq. 4). Amphibole continues to melt partially at H_2O contents in melt less than 4.5 percent, but H_2O produced by its dehydration is greater than that required to enter the amount of liquid produced by its melting.

7. Petrologic applications

The maximum temperature stability limit of amphibole determined at 5.5 kb, 940°C, is probably applicable to most calcalkaline melts. Because the maximum amphibole-out curve (fig. 4c) has a very steep slope, 950°C probably is the upper temperature limit of amphibole stability in calcalkaline melts whose fluid phase contains only H_2O and CO_2 at depths less than 35 km. It is possible that the halogens may increase amphibole stability, however.

Amphibole is also a possible index to H_2O content of calcalkaline melts. The presence of amphibole phenocrysts cannot of itself indicate H_2O content, because the upper stability limit of amphibole may change very little with wide variations in $X^{fl}_{H_2O}$ (fig. 4c). However, while the amphibole-out curve may change very little with $X^{fl}_{H_2O}$, the other silicate liquidi change considerably in temperature isobarically and may lie above or below the amphibole-out curve for a particular $X^{fl}_{H_2O}$. For example, in Paricutin andesite the plagioclase liquidus is higher in temperature than the family of amphibole-out curves unless H_2O content in melt is more than 6 percent [16]. Petrographic criteria indicating coexisting plagioclase and amphibole phenocrysts in an andesite of that composition would be strong evidence that H_2O content in the magma was near 6 percent.

The principles of amphibole stability developed for andesite melt are undoubtedly applicable to basalt melt. The H_2O-undersaturated partial melting of amphibole-bearing basalt may play a very important role in generation of the calc-alkaline suite [3]. This study affirms the possibility of such a mechanism, since amphibole is shown to exist near or above its H_2O-saturated stability limit in silicate melts over a wide range of water-undersaturated conditions. Indeed, fig. 4c suggests that at 9 kb amphibole may be as stable when $X^{fl}_{H_2O}$ = 0.3 as when $X^{fl}_{H_2O}$ = 1.0.

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