Chemical Geology 392 (2015) 1–8

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

A K-feldspar–liquid hygrometer specific to alkaline differentiated magmas

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ARTICLE INFO

Article history:
Received 19 September 2014
Received in revised form 1 November 2014
Accepted 13 November 2014
Available online 21 November 2014

Editor: D.B. Dingwell

Keywords:
Hygrometer
K-feldspar
Phonolite
Trachyte
Phlegrean Fields

ABSTRACT

We present a K-feldspar–liquid hygrometer specific to alkaline differentiated magmas that is calibrated through the regression analysis of sanidine and anorthoclase crystals coexisting with trachyte and phonolite melts. Partial-regression leverage plots were used to determine the minimum number of regression parameters that closely describe the variance of the dataset. The derived model was tested using K-feldspar–liquid pairs not included into the calibration dataset in order to address issues of systematic errors. When K-feldspar and plagioclase crystals coprecipitate from the same alkaline liquid under identical P-T-X-fO_2-H_2O conditions, the ability prediction of the new hygrometer is comparable to that of previous plagioclase–liquid models. To minimize the error of H_2O estimate caused by the inadvertent use of disequilibrium data in natural samples, we have also calibrated a new test for equilibrium based on Or–Ab exchange between K-feldspar and coexisting melt. As an immediate application for both equilibrium and hygrometer models, we used as input data K-feldspar–liquid pairs from alkaline explosive eruptions at the Phlegrean Fields. The estimates of H_2O dissolved in natural trachyte and phonolite magmas closely match those determined by melt inclusion analysis and H_2O solubility modeling. This leads to the conclusion that our new models can significantly contribute to a better quantitative characterization of the H_2O content in differentiated alkaline magmas feeding large-volume explosive eruptions.

1. Introduction

Over the years, several hygrometers have been constructed using plagioclase–liquid exchange between anorthite and albite components (Housh and Luhr, 1991; Putirka, 2005, 2008; Lange et al., 2009). These models are widely applied since plagioclase crystallizes in basalts through rhyolites over a large range of temperatures, pressures, and H_2O concentrations. However, in alkaline differentiated magmas, the stability of plagioclase is drastically reduced or suppressed due to abundant K-feldspar crystallization. For example, the plagioclase:K-feldspar ratio in trachytes is 1:10 or even lower, whereas plagioclase is frequently lacking in phonolites (e.g., Ablay et al., 1995; Fulignati et al., 2004). Under crustal pressures (0.1–0.3 GPa), K-feldspar typically equilibrates at temperatures lower than those of olivine, clinopyroxene and magnetite, but H_2O exsolution from 7 to 2 wt.% increases the first appearance of K-feldspar from 800 to 925 °C (Andujar et al., 2010). The overall crystal content of trachytic and phonolitic magmas remains lower than 7 wt.% until K-feldspar crystallizes and then the crystallinity increases up to 50 wt.% due to prevalent K-feldspar formation (Andujar et al., 2008, 2010; Andujar and Scaillet, 2012). As a result, the magmatic system undergoes important chemical and physical changes (e.g., density, dissolved H_2O content, viscosity and volume fraction fluid; see Fowler et al., 2007), potentially leading to violent explosive eruptions and voluminous caldera-forming events (e.g., Pappalardo et al., 2008; Palladino et al., 2014).

Since H_2O is one of the most important parameters involved with highly explosive eruptions, we present in this study a new K-feldspar–liquid hygrometer specific to alkaline differentiated magmas. The calibration dataset consists of sanidine and anorthoclase in equilibrium with trachytic and phonolitic liquids. Tests performed on a sample population of the dataset demonstrate the reliability of the new hygrometer in predicting melt–H_2O contents. To minimize the error of estimate caused by the accidental use of disequilibrium data, a new equilibrium model between K-feldspar and coexisting liquid has also been calibrated and tested. Both the new hygrometer and equilibrium models are reported as a spreadsheet available as supplementary material. Application of the models to explosive eruptive products at the Phlegrean Fields provides values that closely match the H_2O contents

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http://dx.doi.org/10.1016/j.chemgeo.2014.11.010
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measured in melt inclusions and with calculated H_2O solubility values in trachytic and phonolitic magmas.

2. Dataset, component calculation and regression strategy

The dataset used to calibrate both the new hygrometer and feldspar–liquid equilibrium models consists of K-feldspar–liquid pairs obtained through phase equilibrium experiments on alkaline differentiated magmas (Table 1EA). The experimental data from these previous studies encompass the range of conditions of P = 0.05–0.3 GPa, T = 700–950 °C, H_2O = 2–9.5 wt.% and fO_2 = QFM–NNO + 1.5 (i.e., Andujar et al., 2008, 2010; Fabbrizio and Carroll, 2008; Andujar and Scaillet, 2012; Masotta et al., 2013). As a whole, the calibration dataset comprises a wide range of trachyte and phonolite melts (SiO_2 = 57.8–69 wt.% and $Na_2O + K_2O$ = 10.9–16.1 wt.%; Table 1EA and Fig. 1a) in equilibrium with sanidine and anorthoclase feldspars ($Ab_{16–71}$, $An_{0–12}$ and $Or_{19–84}$; Fig. 1b).

Component calculations were performed following the procedure reported by Putirka (2008). Liquid components have been treated as cation fractions of the oxides SiO_2, TiO_2, $AlO_{1.5}$, FeO, MnO, MgO, CaO, $NaO_{0.5}$, $KO_{0.5}$, and $PO_{2.5}$. The H_2O content of the melt was excluded from the liquid component calculation, and is considered as a dependent variable with units of wt.%. The amounts of K-feldspar components were calculated from cation fractions as $An^{kfs} = [Ca/(Ca + Na + K)]^{kfs}$, $Ab^{kfs} = [Na/(Ca + Na + K)]^{kfs}$, and $Or^{kfs} = [K/(Ca + Na + K)]^{kfs}$.

Preliminary linear least square analyses were conducted using experimental temperatures, pressures and compositions reported in both the calibration and test datasets (Table 1EA). This strategy ensured that regression parameters with high degrees of correlation were correctly identified (Table 1). More complex and statistical parameters for liquid, K-feldspar and K-feldspar–liquid exchange were also considered for the fits, e.g., $\ln[Si \times (Ti + Mg)]^{liq}$, $\ln[(Si \times Ca)/(Fe + Ca)^2]^{Kfs}$ and $\ln[(Or^2)^{Kfs}/(Ca \times K)^{liq}]$ (Tables 1). As a result of these plots, we selected the independent variables for multiple linear regression analyses with high correlation coefficients (R) and low standard errors of estimate (SEE) (Table 2). To test if these variables were indeed independent or, alternatively, were highly correlated providing unreliable regression parameters (i.e., multicollinearity), we used the variance inflation factor (VIF). This statistic test indicates how much the variance of a coefficient is inflated because of linear dependence with other predictors. VIF is always greater than or equal to 1 and values that exceed 10 are often regarded as indicating multicollinearity (Hair et al., 1995). The predictive model presented in this study was then developed (i) using only the calibration dataset reported in Table 1EA, (ii) excluding all variables producing data overfitting (Ratkowsky, 1990; Jefferys and Berger, 1992), and (iii) including the minimum number of independent variables that closely described the variance of the dataset (Putirka, 1999). Through the statistical formula for the standardized regression coefficient, we also determined the influence of each independent variable on the ability prediction of the model; specifically, the standardized regression coefficient equals the original unstandardized regression coefficient of the independent variable (Table 2), multiplied by the standard deviation of the independent variable (Table 1) and divided by the standard deviation of the dependent variable (Table 1).

The new hygrometer was tested by means of two independent datasets not included in the original calibration dataset (Table 1EA). The first dataset consists of phase equilibrium compositions subtracted to the calibration dataset and obtained in laboratory by the same authors (i.e., Andujar et al., 2008, 2010; Fabbrizio and Carroll, 2008; Andujar and Scaillet, 2012; Masotta et al., 2013). The second dataset comprises K-feldspar–liquid pairs recovered through MELTS (Ghiorso and Sack, 1995) numerical simulations that were carried out at P-T-X-fO_2-H_2O conditions comparable to those of laboratory experiments, i.e., 0.10–0.30 GPa, 786–1007 °C, 1.8–8.0 wt.% H_2O and QFM–NNO + 0.5 buffers, using trachytic and phonolitic starting compositions (Table 1EA). This latter test was encouraged by recent studies that demonstrated a fairly good agreement between phase relationships and compositions predicted by MELTS and those observed in natural and experimental trachyte and phonolite products (e.g., Fowler et al., 2007; Masotta et al., 2010). The MELTS code is based on an independent set of thermodynamic data for mineral phases and its outputs are the result of thermodynamic algorithms for detection of phase saturation and energy convergence (e.g., Gibbs free energy minimization; Ghiorso and Sack, 1995). Conversely, empirical models coincide with the fit of laboratory data that is used to retrieve statistically significant regression parameters (cf. Putirka, 2008). In view of these very different kinds of calibrations, Armienti et al. (2013) suggested that the convergence between MELTS and empirical models and their independent estimates of melt–H_2O contents is a useful test to assess whether or not both models are internally consistent.

We also determined the error of H_2O estimate (EWE) caused by the inclusion of rhyolitic data that are significantly different from the trachytic and phonolitic compositions recommended for the new hygrometer. According to previous studies, EWE is expressed as the difference between the concentration of H_2O measured in the melt and that predicted by the model (Putirka, 2008; Masotta et al., 2013; Mollo et al., 2013). This test is very useful to ascertain the limits of the model and to evaluate the uncertainty that should be expected by the use of highly evolved K-feldspar–liquid pairs.

3. Results and discussion

3.1. Calibration, test, and limit of the hygrometer

With respect to the liquid components, i.e., Al^{liq}, Fe^{liq}, Ca^{liq} and Na^{liq}, used for the calibration of previous plagioclase–liquid hygrometers

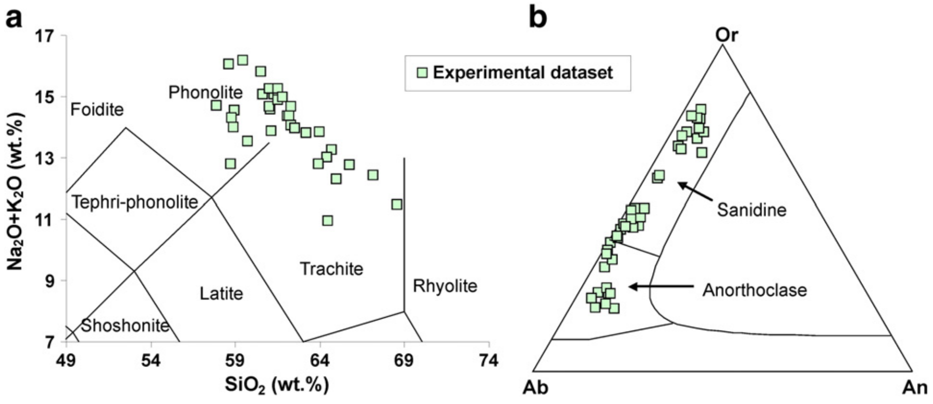

Fig. 1. Total alkali versus silica diagram (a) and ternary phase diagram for the system Or–Ab–An (b) showing liquids and K-feldspars from the alkaline dataset, respectively.