A method to estimate the pre-eruptive water content of basalts: application to the Wudalianchi–Erkeshan–Keluo volcanic field, Northeastern China

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Abstract

Water plays an important role in the generation and evolution of volcanic systems. However, the direct measurement of the pre-eruption water content of subaerial volcanic rocks is difficult, because of the degassing during magma ascent. In this study, we developed a method to calculate the pre-eruption water content of the basalts from the Cenozoic Wudalianchi–Erkeshan–Keluo (WEK) potassic volcanic field, Northeastern China, and investigated their mantle source. A water-insensitive clinopyroxene–melt thermobarometer and a water-sensitive silica activity thermobarometer were applied to these basalts. Two pressure–temperature ($P–T$) paths of the ascending magma were calculated using these two independent thermobarometers, with a similar $P–T$ slope but clear offset. By adjusting the water content used in the calculation, the difference between the two $P–T$ paths was minimized, and the water content of the WEK melts was estimated to be $4.5 \pm 1.2$ wt% at a pressure range of $10.1–13.5$ kbar, corresponding to depths of $37–47$ km. Degassing modeling shows that during the magma ascent from below the Moho to near the surface, CO$_2$ was predominantly degassed, while the melt H$_2$O content kept stable. Significant H$_2$O degassing occurred until the magma ascended to $5–2$ kbar. The silica activity $P–T$ estimates of the most primary WEK samples suggest that the magmas were generated by the melting of convective mantle, which was probably facilitated by a wet upwelling plume from the mantle transition zone. The high water content found in the WEK basalts is similar to the recent reports on Phanerozoic intraplate large igneous provinces (LIPs), and supports the presence of hydrated deep mantle reservoirs as one
possible source of the LIPs.

Keywords: water content, potassic basalt, degas, thermobarometer, Northeastern China, Wudalianchi–Erkeshan–Keluo

Introduction

Water plays an important role in terrestrial and planetary magmatic processes (Hirschmann 2006; O’Neill et al. 2007; Wilson 2009; Ni et al. 2016; Peslier et al. 2017). In the source mantle, water controls the two most important factors constraining the primary melt composition: the depth and degree of melting (Katz et al. 2003; Asimow and Langmuir 2003). During magma ascent, the exsolution of water can trigger vesiculation and change the fluid dynamics of the volcanic system (Gonnerman and Manga 2007). During the eruption, water can control the explosiveness and flow regime (Wilson 1980, 2009; Kieffer 1995). Thus, the water contents of magmas, especially the water contents of primary melts, have long been investigated.

For magmas erupted on the deep seafloor, the primary water content can be acquired by direct analysis of glass (e.g., Michael 1995; Dixon et al. 1997; Hauri et al. 2002). For subaerially erupted volcanic rocks, however, the estimation of the primary water content is difficult due to the ubiquitous escape of volatiles during the eruption. Primary melt inclusions are believed to be a good indicator of the pre-eruption water content (e.g., Hauri 2002; Dixon and Clague 2001); however, these inclusions are very
rare and easily altered by the interaction with the host minerals (Chen et al. 2011; Gaetani et al. 2012). Another method is to measure the water content of clinopyroxene phenocrysts and calculate the melt water content using a partitioning coefficient \([K_{D}(H_2O)_{cpx-melt}]\) (e.g., Wade et al. 2008; O’Leary et al. 2010), which, however, is not applicable at all times as the water content of clinopyroxene decreases owing to the diffusive re-equilibration with the melt during ascent-driven degassing (Cashman 2004; Lloyd et al. 2016; Turner et al. 2017). Due to the diffusive water loss, both the melt inclusion and phenocryst methods provide a minimal estimation of the pre-eruption water content of the melt. Therefore, an ideal method of water content estimation for melts that have experienced water exsolution is still required.

In this study, we develop a new method to determine the pre-eruption water contents of melts by combining a water-insensitive and a water-sensitive thermobarometer. The water-insensitive thermobarometer is based on the clinopyroxene–melt equilibrium (Putirka et al. 2003) and has been widely applied for the pressure–temperature (P–T) estimation of magmas with variable water contents (e.g., Putirka 1997, 2008; Putirka et al. 2009, 2012; Wang et al. 2012; Armienti et al. 2013). Another popular thermobarometer, first established by Carmichael et al. (1970) and recalibrated by Lee et al. (2009), is based on the Si activity in the olivine–melt–orthopyroxene equilibrium system and is water-sensitive. Theoretically, these two thermobarometers should give identical P–T estimates, i.e., they should plot onto a common P–T trajectory when applied to the same volcanic field. Thus, we can obtain the water content of the melt by
fitting these two suites of $P$–$T$ estimates into a common $P$–$T$ trajectory. The water content fitted by the thermobarometers can represent the actual quantity of water in the melt prior to degassing.

Recently, the Cenozoic continental flood basalt (CFB) province in Central-East Asia has been of interest to many researchers, owing to the arguments over whether it is the product of dry melting of the hot upwelling mantle or of wet melting of the transition-zone mantle hydrated by slab stagnation (Wang et al. 2015). The Wudalianchi–Erkeshan–Keluo (WEK) potassic volcanic field, NE China, is the youngest representative of this CFB province. Some researchers suggest that the WEK potassic basalts have a relatively low water content (Chen et al. 2015), while others argue that the basalts were derived from the melting of the highly hydrous transition-zone mantle (Kuritani et al. 2013). Here we apply the clinopyroxene–melt thermobarometer (Putirka et al. 2003) and the Si activity thermobarometer (Lee et al. 2009) to the WEK volcanic rocks, with the aims of estimating the water content of the WEK melts prior to degassing and constraining their source mantle.

**Geological setting**

Cenozoic intraplate volcanic activity has occurred widely in Northeastern China (Fig. 1). These eruptions began in the Late Cretaceous and have continued until recent human history (Liu et al. 2001). Over 590 volcanic edifices and ~50,000 km$^2$ of surface lava flows are distributed along the NNE/NE trending rift-graben systems (Zhou et al.
Their compositions range from tholeiitic to alkaline basalts, with more evolved trachybasalts, trachytes, and phonolites. These volcanic rocks have been regarded either as a result of the replacement of the ancient lithosphere by new, oceanic mantle (Xu et al. 2005, 2012; Tang et al. 2006) or related to the stagnation of the Pacific slab in the mantle transition zone (Sakuyama et al. 2013; Kuritani et al. 2011, 2013; Wang et al. 2015).

As one of the major alkaline volcanic rock fields in Northeastern China, the Wudalianchi–Erkeshan–Keluo (WEK) volcanic field (Basu et al. 1991; #5 in Fig. 1) has drawn special attention because of its highly potassic magma compositions (Zhang 1984; Qiu 1991; Basu et al. 1991; Zhang et al. 1995, 1998; Zou et al. 2003; Chen et al. 2007; Kuritani et al. 2013; Chu et al. 2013; Sun et al. 2014, 2015, 2017; Zhao et al. 2014a, 2014b; Liu et al. 2016; Tian et al. 2016; Wang et al. 2017). Recent studies also demonstrated that this potassic volcanic field may extend to the adjacent Xiaogulihe site (Shao et al. 2009; Sun et al. 2014). The WEK volcanoes erupted potassic magmas including olivine leucitite, leucite basanite, and trachybasalt, at three episodes during Miocene (9.6–7.0 Ma), middle Pleistocene (0.56–0.13 Ma), and recent human history (1719–1721 A.D.; Zhang et al. 1995).

The WEK volcanic field contains substantial scoria cones with height/base diameter ratios of ~0.2 (Zhao et al. 2014b). The lava flows are characterized by abundant elongated vesicles as well as volcanic bombs on the flow surfaces (Fig. 2c). These field characteristics indicate that the eruption styles of the WEK volcanoes were mainly
Strombolian type. Many mantle xenoliths are enclosed in the WEK basalts (Zhang et al. 2000, 2011; Chen et al. 2007).

**Sample description**

Twenty-six lava flow samples (Table S1 in the Supplemental Materials) were collected from the flow fields of Yaoquanshan volcano (acronym in Table S1: YQ; same as below), the proximal area of Laoheishan volcano (LHS), the distal area of Laoheishan volcano (SC), Huoshaoshan volcano (HSS), the distal area of Jiaodebu volcano (GST), Erkeshan volcano (KD), and Dayishan volcano (KL). We present major- and trace-element results and Sr–Nd isotope data for all the 26 samples in Tables S1 and S2. Eight samples were analyzed in this study; the remaining 18 were reported in Chu et al. (2013). Mineral chemistry of clinopyroxene for six representative samples are listed in Table S3. The detailed methodology is described in Appendix A in the Supplemental Materials.

Photographs of representative samples are provided in Fig. 2. Based on mineral mode compositions, the WEK potassic volcanic rocks are classified as olivine leucitites, leucite basanites, and trachybasalts. The volcanic rocks are aphyric and glassy, containing a small proportion of phenocrysts (<5%). These phenocrysts are less than 0.5 mm in diameter and consist of olivine, clinopyroxene, and leucite. The presence of euhedral olivine and clinopyroxene phenocrysts, together with melt inclusions, suggests a magmatic rather than xenocrystic origin (Chu et al. 2013). Most clinopyroxene
phenocrysts do not show detectable zoning; some occasional oscillatory zoning (Fig. 2a) observed indicates the normal pattern of crystal growth (Shore and Fowler 1996). The embayment structure of olivine (Fig. 2d) indicates rapid decompression (Kuritani et al. 2013). The matrix mainly consists of quenched glass, olivine, clinopyroxene, K-feldspar, and minor oxide minerals. Elongated bubbles, a typical gas-rich eruption feature, ubiquitously occur in our samples (Figs. 2b, 2c). Mantle-derived peridotite xenoliths and xenocrysts are present at each volcanic site.

On the total alkali–silica (TAS) diagram (Fig. S1), the WEK volcanic rock samples plot in the areas of potassic phonolite, tephriphonolite, basaltic trachyandesite, and trachyandesite. Although chemical classification shows that the WEK volcanic rocks are not basalts, they have been consistently referred to as “potassic basalts” since Basu et al. (1991). For consistency and simplicity, we adopt “potassic basalt” as a generalized name for the WEK volcanic rocks.

**Thermobarometric methods**

**Clinopyroxene–melt thermobarometer**

The thermobarometer of Putirka et al. (2003) was applied to our WEK samples. This thermobarometer was calibrated based on the jadeite–melt and jadeite–diopside + hedenbergite exchange equilibrium thermodynamics, and the calibration dataset covers a wide range of pressure (up to 35 kbar), temperature (850–1300 °C), and composition (including Si-rich, alkali-rich, and hydrous melts). In our $P–T$ calculations, the
clinopyroxene compositions were paired with their corresponding bulk-rock compositions. For large clinopyroxene phenocrysts, multiple analytical spots were treated individually. The standard estimate error (SEE) is 33 °C for temperature and 1.7 kbar for pressure (Putirka et al. 2003).

There are several ways to test the equilibrium between clinopyroxene and melt (see Appendix B in the Supplemental Materials for details); herein the Fe–Mg exchange test was used before \( P - T \) calculation. The Fe–Mg exchange coefficient between clinopyroxene and the equilibrated melt \( [K_D(\text{Fe–Mg})_{\text{cpx–melt}} = \frac{(\text{Fe}/\text{Mg})_{\text{cpx}}}{(\text{Fe}/\text{Mg})_{\text{melt}}}, \) where Fe and Mg are in molar fraction] derived from 1,245 experimental observations yields a roughly normal distribution ranging from 0.04 to 0.68, with a mean value of 0.28 and standard deviation (\( \sigma \)) of 0.08 (Putirka 2008). Using this criterion at 2\( \sigma \) level, 78 (out of 122) equilibrated clinopyroxene–melt pairs with \( K_D(\text{Fe–Mg})_{\text{cpx–melt}} \) between 0.12 and 0.44 were selected. All these clinopyroxene grains have Mg\# > 75 [Mg\# = 100\( \times \)Mg/(Mg+Fe), where Fe and Mg are in molar fraction]. We plot the clinopyroxene and bulk-rock Mg\# values in the Rhodes’ diagram (Rhodes et al. 1979) (Fig. 3a) to illustrate this equilibrium test. Nearly all the phenocrysts (including multi-spot analyses on zoned phenocrysts) are in equilibrium with their host rocks. However, most groundmass clinopyroxene grains exhibit disequilibrium features, suggesting that they formed after significant magma crystallization, perhaps during the surface lava evolution. Clinopyroxene grains that are not in equilibrium with their host rocks were excluded in the \( P - T \) estimation.
The host bulk-rock composition of each clinopyroxene crystal was assumed as the melt composition in our calculation, because the compositional evolution of the melt due to crystallization is found to be negligible. The area analysis of thin-sections indicates that phenocrysts (diameter ≤ 0.5 mm) occupy less than 5% of the thin-section area, making their contribution to the modification of the melt composition insignificant. In addition, the Mg# values of low-pressure clinopyroxene grains do not show a marked decrease when compared to the higher-pressure ones (Fig. 3b). The groundmass clinopyroxene grains have lower Mg# (Fig. 3a), but their crystallization occurred after the crystallization of the high-Mg# phenocrysts. Therefore, the crystallization of groundmass clinopyroxene grains could not have influenced the composition of the melt at deeper depths. Finally, the melt-equilibrated clinopyroxene compositions simulated using the models of Putirka (1999) at the $P–T$ conditions obtained from thermobarometry are identical to the measured clinopyroxene compositions within the prediction errors (Fig. 3c).

**Si activity thermobarometer**

The Si activity thermobarometer of Lee et al. (2009), which was calibrated based on the thermodynamics of $\text{SiO}_2(\text{melt})–\text{Mg}_2\text{SiO}_4(\text{olivine})–\text{MgSiO}_3(\text{orthopyroxene})$ equilibrium, was applied to our samples. This thermobarometer was calibrated over a wide range of pressure (up to 7 GPa), temperature (1100–1800 °C), and composition (including Si-rich, alkali-rich, low-Mg#, and hydrous melts). The application of this
A major prerequisite for using the Si activity thermobarometer is that the melts are in equilibrium with both olivine and orthopyroxene. The source mantle lithology of the WEK basalts is dominated by peridotite rather than pyroxenite, based on the low Fe/Mn ratios of olivine phenocrysts (Sun et al. 2014 and our unpublished data). In addition, the mantle xenoliths recovered in the WEK lava consist of lherzolites and harzburgites (Zhang et al. 2011). Therefore, the Si activity of the WEK melts tend to be consecutively buffered by olivine and orthopyroxene during the mantle-level evolutions, such as partial melting (polybaric or monobaric) and re-equilibration at shallower depths (Lee et al. 2009; Plank and Forsyth 2016). Crustal assimilation and fractional crystallization, however, can alter the equilibrated melt composition and cause underestimations of pressure and temperature (Putirka et al. 2012; Plank and Forsyth 2016). The WEK basalts have not experienced significant crustal assimilation, as evidenced by the rapid magma ascending rates indicated by the occurrence of mantle xenoliths and significant $^{230}$Th excesses (Zou et al. 2003), the uncontaminated mantle Os isotope and platinum group element signatures (Chu et al. 2013; Sun et al. 2014), and the limited interactions between crust xenoliths and the host lava (McGee et al. 2015). Fractional crystallization of olivine may
have occurred, but the degree is restricted to have negligible effects in generating the observed magma composition variations (Zhang et al. 1995; Kuritani et al. 2013; Wang et al. 2017). Thus, in principle, these basalts should have nearly mantle-equilibrated signatures as exemplified by their high Mg#. We compiled 127 reliable WEK basalt compositions with ferrous/ferric ratios from the literature (Qiu 1991; Zhang 1984). The Fe$^{3+}$/($Fe^{3+}+Fe^{2+}$) ratio shows a logarithmic normal distribution, with an expected value of 0.28. Using this Fe$^{3+}$/($Fe^{3+}+Fe^{2+}$) ratio, we got better constrained Mg# values of 67–74 for our WEK samples. Combined with Tamura et al. (2000)’s composition-dependent $K_D$(Fe–Mg)$_{ol-melt}$, the olivine crystals in equilibrium with most WEK basalts (except sample YQ4) have Fo values [Fo = 100×Mg/(Mg+Fe), where Fe and Mg are in molar fraction] ranging from 87 to 90, falling into the range of mantle xenolith olivine grains discovered in this area (Zhang et al. 2000). Therefore, our WEK samples are likely to be in equilibrium with the olivine and orthopyroxene in the proximal mantle, and the crust-level evolutions should be negligible.

Another Si activity barometer, calibrated by Putirka (2008) based on the same thermodynamic equilibrium but with a different Si activity expression and experimental dataset (in similar $P$, $T$, melt composition, and $H_2O$ ranges), was used to cross-check the pressure estimates. With the same temperature inputs, the two independent barometers yielded identical pressure estimates for our WEK basalts (Fig. 3d). This agreement provides additional confidence for our $P$–$T$ estimates.
Results

Clinopyroxene–melt thermobarometer

The $P-T$ results of the clinopyroxene–melt thermobarometer are listed in Table S3 (in the Supplemental Materials) and plotted as blue circles in Fig. 4a. The clinopyroxene and the melt equilibrated at a pressure range of 0.8–13.5 kbar and a temperature range of 1051–1162 °C. The $P-T$ results exhibit a linear trend of $P/kbar = -118.0 + 0.113 T/°C$ ($R^2 = 0.85$).

Si activity thermobarometer

The $P-T$ results of the Si activity thermobarometer are illustrated in Fig. 4a. The $H_2O$ content of 0.50 wt% yields pressures between 8.8 and 15.5 kbar (corresponding to depths of 33–54 km) and temperatures between 1129 and 1260 °C, and the $H_2O$ content of 1.4 wt% yields pressures between 9.1 and 15.6 kbar (corresponding to depths of 34–54 km) and temperatures between 1124 and 1247 °C. The $P-T$ estimates from this thermobarometer also exhibit linear trends, with a slope similar to that of the clinopyroxene–melt thermobarometer. However, the intercepts with the $T$-axis of both Si activity $P-T$ arrays are different from that of the clinopyroxene–melt array.

Melt water content estimation

The plot of $P-T$ results is generally divided into three pressure ranges (Fig. 4a): the lower-pressure range determined only by the clinopyroxene–melt thermobarometer; the
higher-pressure range determined only by the Si activity thermobarometer; and the
overlapping pressure range in which both thermobarometers yielded $P$–$T$ results. The
overlapping pressure range of two thermobarometers are from 8.8 to 13.5 kbar when the
0.50 wt% H$_2$O content is used, and from 9.1 to 13.5 kbar when the 1.4 wt% H$_2$O content
is used. At the overlapping pressure ranges, the temperatures estimated by the
clinopyroxene–melt thermobarometer tend to be systematically lower than those of the Si
activity thermobarometer.

There is only one real $P$–$T$ path for the magmas, and both the thermobarometers
should reproduce this real $P$–$T$ path. The clinopyroxene–melt thermobarometer (Putirka
et al. 2003) is independent of H$_2$O content, and hence the $P$–$T$ path calculated by this
thermobarometer would represent the real $P$–$T$ path within its SEE. However, the Si
activity thermobarometer of Lee et al. (2009) is water-sensitive. A higher H$_2$O content
used in the calculation can effectively increase the pressure but decrease the temperature,
as demonstrated by the contrast between the $P$–$T$ paths calculated using the 1.4 wt% and
the 0.50 wt% H$_2$O content (Fig. 4a). When the actual melt H$_2$O content is used in the
calculation, the Si activity thermobarometer should generate a $P$–$T$ path consistent with
the clinopyroxene–melt thermobarometer, i.e., both thermobarometers should generate
identical temperature estimates at the same pressure range. The observed offsets between
the $P$–$T$ paths of the two thermobarometers in the overlapping pressure ranges (Fig. 4a)
therefore indicate that the H$_2$O contents used in the Si activity thermobarometer (0.50 wt%
and 1.4 wt%) may not represent the actual melt H$_2$O content. In contrast, the H$_2$O content
that minimizes the difference between the two $P$–$T$ paths should be close to the actual amount of water dissolved in the melt at the overlapping pressure range.

The temperature difference at the same pressure ($|\Delta T|$) between the $P$–$T$ results of the two thermobarometers varies with the $\text{H}_2\text{O}$ content used in the calculation of the Lee et al. (2009) thermobarometer (Table 1). We note that $|\Delta T|$ is minimized when the $\text{H}_2\text{O}$ content approaches ~5 wt%. Therefore, it is reasonable to suppose ~5 wt% as the actual melt $\text{H}_2\text{O}$ content in the overlapping pressure range of 10.3–13.5 kbar (Table 1). However, this temperature difference is only a qualitative indicator based on the arbitrary judgment of scattered data points. For most of the cases, due to the lack of a perfect match in pressure, this arbitrary point-fitting method may not work well.

We instead propose to use a single parameter, “buffer overlapping area (BOA)”, to evaluate the offset of the two $P$–$T$ paths as a function of $\text{H}_2\text{O}$ content. To construct a buffer for a thermobarometer, the error ellipse of each $P$–$T$ point estimated by this thermobarometer was drawn on the $P$–$T$ plot. The fields covered by these ellipses were then outlined to form one (or more) closed shape(s), which is called a buffer. We constructed buffers for the clinopyroxene–melt thermobarometer and the Si activity thermobarometer (Fig. 4a) following this procedure. The overlapping “area” of the two buffers in the $P$–$T$ space, BOA, can be calculated when the $\text{H}_2\text{O}$ content used in the Si activity thermobarometer is known (details of the BOA calculation are given in Appendix C in the Supplemental Materials). It is clear that, the smaller is the difference of the two $P$–$T$ paths, the larger is the BOA. Thus, when the BOA is maximized, the difference of
the two $P$–$T$ paths is minimized. We calculated BOA values at $H_2O$ contents from 0 wt% to 9 wt% with increment of 0.1 wt%. The maximal BOA (BOAmax) was obtained for an $H_2O$ content of 4.5 wt%. In Fig. 4b, we plot the BOA/BOAmax ratio against the melt $H_2O$ content used in the Si activity thermobarometer. This ratio reaches unity (BOA/BOAmax = 1) when $H_2O = 4.5$ wt%, as expected. When the $H_2O$ content is below or above this value, BOA/BOAmax decreases gradually. Therefore, 4.5 wt% is taken as our best estimate for the pre-eruptive WEK melt $H_2O$ content at the overlapping pressure range of 10.1–13.5 kbar (corresponding to depths of 37–47 km).

Quantifying the uncertainty of our estimate of the $H_2O$ content, however, is not explicit, because it has no direct error propagation relationship from the uncertainties of the thermobarometers. Moreover, the systematic error in our estimation has not been examined. Evaluation of the reliability and accuracy of our $H_2O$ content estimation method can be done with an experimentally-derived dataset of hydrous compositions. We compiled twenty-one sets of experimental data with equilibrium phase assemblages of $\text{melt} + \text{olivine} + \text{clinopyroxene} + \text{orthopyroxene} \pm \text{other phases}$ and $1 \leq H_2O^{\text{melt}} \leq 7$ wt% from the Library of Experimental Phase Relations database (LEPR, Hirshmann et al. 2008) and summarize them in Table 2. For each set of equilibrium phases, we estimated the $P$–$T$ conditions using the two thermobarometers, and then calculated BOAs with $H_2O$ content changing from 0 to 9 wt% with 0.1 wt% increment. In this case, a buffer is simply an error ellipse instead of a closed shape formed by multiple ellipses. The melt $H_2O$ content was estimated as the $H_2O$ content that maximizes the BOA, i.e., when the $P$–$T$
estimates of the two thermobarometers are the closest. Fig. 5a shows estimated versus measured melt H$_2$O contents for the experimental equilibria. The H$_2$O content estimates scatter near the 1:1 line, indicating no significant systematic error in our estimation. Our method reproduces the experimental melt H$_2$O contents with standard estimate error [standard estimate error (SEE) = $\sqrt{\sum(X_{est} - X_{true})^2/N}$, where $X_{est}$ is the estimated value, $X_{true}$ is the true value, N is the number of data] of 1.2 wt%. Using the estimated H$_2$O contents, the Si activity thermobarometer also reproduces the experimental $P$–$T$ conditions (Fig. 5b and 5c), confirming the inter-consistency of the models. Therefore, we take the SEE of 1.2 wt% as an indicative uncertainty for our H$_2$O content estimate of the WEK melts. This SEE may be further justified with larger testing datasets, and be improved with better calibrations of thermobarometers.

The saturation temperature of clinopyroxene is controlled by the melt H$_2$O content at a given pressure. All the WEK basalts are nearly aphyric with trace amount (<5 % area in thin section) of clinopyroxene microphenocrysts, suggesting that the clinopyroxene grains had crystallized when the magma temperatures were close to the clinopyroxene saturation temperatures. By using the equation (34) of Putirka (2008), we calculated the clinopyroxene saturation surfaces of a typical WEK potassic basalt sample, HSS5, at different H$_2$O contents. The $P$–$T$ path of the WEK magmas is roughly parallel to the clinopyroxene saturation surfaces. At >5 kbar, nearly all the clinopyroxene–melt $P$–$T$ estimates are located between the clinopyroxene saturation surfaces with 4 and 5 wt% H$_2$O (Fig. 4a). Such high H$_2$O contents are notably consistent with our estimate acquired
from the dual-thermobarometer method. This result also indicates that, nearly no decrease 
of the melt H$_2$O content occurred during the magma decompression from 13.5 to 5 kbar.

Discussion

Elevated $dT/dP$ of the magma and H$_2$O–CO$_2$ degassing

The linear regression of the $P$–$T$ array of the WEK magma yielded a $dT/dP$ value 
of 8.8 °C/kbar (Fig. 4a). However, a basaltic magma isentropically (i.e., reversibly and 
adiabatically) ascending through the lithosphere follows a $P$–$T$ trajectory with $(\partial T/\partial P)_S \approx 
3.3$ °C/kbar [or $(\partial T/\partial z)_S \approx 1.0$ °C/km, McKenzie and Bickle 1988; $(\partial T/\partial P)_S$: $dT/dP$ when 
the entropy is constant; $(\partial T/\partial z)_S$: $dT/dz$ when the entropy is constant]. When the magma 
ascends adiabatically but irreversibly (e.g., rapid ascending process), the $(\partial T/\partial P)_{Q,ir}$ value 
[$(\partial T/\partial P)_{Q,ir}$: $dT/dP$ when the heat is zero and the process is irreversible] decreases owing 
to the generation of entropy (Ganguly 2008; Armienti et al. 2013). The isentropical 
decompression slope $(\partial T/\partial P)_S$ is controlled by the thermal expansion coefficient ($\alpha$), 
specific heat capacity ($c_p$), and density ($\rho$) of the system (McKenzie and Bickle 1988). 
Using the $\alpha$, $c_p$, and $\rho$ data listed in Table 3, our calculated $(\partial T/\partial P)_S$ for the volatile-free 
HSS5 melt is 2.5 °C/kbar, close to the recommended value for basaltic melt (McKenzie 
and Bickle 1988) but far lower than the regressed $dT/dP$ value of 8.8 °C/kbar.

The heat loss through magma–wall rock interaction during the magma ascending 
can increase the $dT/dP$ value. However, the exceptionally hot eruption temperature 
(~1250 °C) of the WEK magmas estimated by Kuritani et al. (2013) and the rapid ascent
constrained by significant $^{230}$Th excesses (Zou et al. 2003) are consistent with extensive magma–wall rock thermal interaction being unlikely. An alternative explanation of this high $dT/dP$ is the exsolution of volatiles, such as H$_2$O and CO$_2$. Significant expansion of fluid during adiabatic decompression can facilitate the cooling of the magma system, leading to a high $dT/dP$ value. As shown in Table 3, to produce such a high adiabatic $dT/dP$ value of 8.8 °C/kbar, the existence of fluid with high $\alpha$ and low $\rho$ is required for the WEK magma system.

The existence of a fluid phase indicates that the magma ascent is accompanied by degassing. The pressure of volatile saturation depends on the contents of major volatile species in the melt, i.e., H$_2$O and CO$_2$. We have no direct constraint on the volatile saturation pressure of the WEK magmas, because the melt CO$_2$ contents are unknown. However, the ubiquitous occurrence of mantle xenoliths in the lava (Zhang et al. 2000) strongly implies that the WEK magmas started degassing at mantle depths, as the entrapment of xenoliths and the high magma transport rate essential for preserving the xenoliths ($10^{-1}$ to several m/s, Spera 1984) require rapid brittle failure (i.e., explosion) of the mantle wall rock, which is most likely triggered by the formation of bubbles (Lensky et al. 2006). Therefore, we assume that the melt dissolving 4.5 wt% H$_2$O is volatile-saturated at 13.5 kbar and 1438 K (the deepest point on the clinopyroxene–melt $P$–$T$ array). At this state, the melt CO$_2$ content is predicted to be 2.0 wt% using the solubility model of Duan (2014). If the pre-degassing melt CO$_2$ content was lower (or higher) than 2.0 wt%, the degassing would start from a lower (or higher) pressure.
shown in Fig. 6, the H$_2$O–CO$_2$ degassing along the $P$–$T$ path of the WEK magmas in both
closed and open systems were simulated using the model of Duan (2014). From the
degassing curves, CO$_2$ was substantially removed from the melt when the pressure drops
from 13.5 kbar to 5 kbar, while the loss of H$_2$O was insignificant. At $P < 5$ kbar, the
degassing behavior of H$_2$O is distinct between closed and open systems: the onset of H$_2$O
exsolution from the melt was earlier in the closed system but later in the open system
until ~2 kbar. It is clear that the melt H$_2$O content of the ascending magma stayed
unchanged during high pressure degassing, which is in good agreement with the
clinopyroxene saturation surface calculation results above (Fig. 4a).

**Constraints on the source mantle**

The most unique geochemical characteristics of the WEK basalts are their
EM1-like Sr–Nd–Hf isotopes, low $\delta^{26}$Mg values, and extremely unradiogenic Pb isotopes
(Zhang et al. 1995; Chu et al. 2013; Sun et al. 2014, 2017; Wang et al. 2017). The
correlations of these features indicate a recycled, isotopically “enriched” component in
the source mantle. However, the interpretation of this enriched component, coupled with
the issue of the ultimate source of the WEK magmas, is being debated. Several competing
theories concerning this problem have been put forward: (1) potassium-rich
sub-continental lithospheric mantle (SCLM) metasomatized by melt/fluid from ancient
asthenosphere (Zhang et al. 1995, 1998, 2000; Zou et al. 2003), delaminated Precambrian
lower crust fragments (Chu et al. 2013), or ancient subducted oceanic crust (Sun et al.
2014, 2015, 2017); (2) sub-lithospheric (or transition zone) mantle metasomatized by (or mixed with) sediment fluid from an ancient stagnant slab (Kuritani et al. 2013), carbonate melt from the modern Pacific slab (Tian et al. 2016), or remnants of an ancient carbonate-bearing slab upwelled from the mantle transition zone (MTZ) (Wang et al. 2017). These conflicting models cannot provide a clear prospect about the real magma source, thus evidence external to geochemical data are needed to constrain the origin of the WEK volcanic rocks.

The source of the magmas can be located by determining the depths of melt generation and transportation. We calculated the pressures and temperatures for six low-SiO$_2$ melts from Zhang et al. (1995) using the Lee et al. (2009) Si activity thermobarometer. Compared to our WEK dataset, these complimentary samples have higher MgO contents (up to 14.40 wt%) and equilibrium Fo values (up to 92.0), thus representing the compositions of more primary melts. They plot on the extrapolation of our regressed $P$--$T$ path and extend to higher $P$ and $T$ (Fig. 7a), suggesting that the WEK melts originated from a deeper mantle. The deepest melt--olivine--orthopyroxene equilibria occurred at 80–110 km (translated from $P = 23$–33 kbar). These depths coincide with the low-velocity asthenosphere underlying the 70–80 km thick high-velocity lithosphere lid from seismological constraints (e.g., Zheng et al. 2011; Li et al. 2012, 2013; Guo et al. 2014), thus clearly indicating that the parental WEK melts were generated beneath the SCLM. These $P$--$T$ estimates lie closely along a hydrous peridotite solidus with $X_{H2O}^{\text{bulk}} = 450$ ppm (calculated using the model of Katz et al. 2003, with
\( X_{\text{H}_2\text{O}}^\text{melt} = 4.5 \text{ wt\%} \) from our estimation and a partitioning coefficient of 0.01), implying that the melts can be generated by small-degree wet melting at these depths. If \( \text{CO}_2 \) has further lowered the peridotite solidus (e.g., Dasgupta et al. 2007), melting may begin at a greater depth, and the observed melt--mantle equilibrium depths may reflect the ponding of melts at the base of the lithosphere. The stalled melts may thermally and chemically erode the overlying lithosphere and cause its degradation (Plank and Forsyth 2016; Putirka et al. 2012). Overall, our inferred melting depths support the geochemical models with a sub-lithospheric mantle origin of the WEK magmas.

The melting of the sub-lithospheric mantle may be related to the mantle upwelling initiated from the MTZ. Recent high-resolution mantle tomography studies have revealed large-scale (deep to \( \sim 400 \) km), vertically continuous low-velocity anomalies beneath WEK and other NE China Cenozoic volcanos (Wei et al. 2019; Ma et al. 2018; Zhao et al. 2009). The nature of this deep mantle upwelling, however, is debated. The upwelling of wet mantle materials from the MTZ (Kuritani et al. 2011, 2013, 2019; Zhao et al. 2009) or a hot mantle plume through a hole at the edge of the stagnant Pacific slab (Tang et al. 2014) have both been proposed for the origin of the deep back-arc volcanisms in NE China. To examine whether excess heat contributed to the mantle upwelling beneath WEK, we calculated the mantle potential temperature (\( T_p \)) using the Putirka (2016) model. The most primary WEK melt compositions passed all the essential equilibrium tests of this model, and yielded an average \( T_p \) of 1372 ± 30 °C. This \( T_p \) is significantly lower than those of the intraplate volcanic hotspots (e.g., Hawaii and Samoa \( T_p = 1722 \) °C, Putirka et
al. 2007; Emeishan $T_p = 1740–1810$ °C, Tao et al. 2015; Siberian Trap $T_p = 1600$ °C, Sobolev et al. 2011), but is similar to the ambient upper mantle temperature represented by the average mid-ocean ridge ($T_p = 1454 \pm 78$ °C, Putirka et al. 2007) and the $T_p$ of wet arc or back-arc mantle in subduction zones (e.g., Mariana arc and trough $T_p = 1350$ °C, Kelly et al. 2010; Yamato Basin, Japan Sea $T_p = 1200–1320$ °C, Hirahara et al. 2015; Changbaishan, NE China $T_p = 1314–1357$ °C, Kuritani et al. 2019). This low-$T_p$ characteristic suggests that the mantle upwelling beneath the WEK area is not an active plume driven by thermal buoyancy, but rather, facilitated by fluids released from the stagnated Pacific slab in the MTZ (Kuritani et al. 2019; Richard and Bercovici 2009; Richard and Iwamori 2010). The “wet plumes” (Iwamori 1991, 1992) may carry water and other fluids from the MTZ to the upper mantle, and lead to wet melting in the asthenosphere (Fig. 7b). This volatile-rich mantle source is consistent with our inferred high H$_2$O (and CO$_2$) contents of the WEK magmas.

Comparison with Xiaogulihe volcanic rocks: implication of mantle H$_2$O heterogeneity

The WEK potassic basalts and the Pleistocene ultrapotassic volcanic rocks from Xiaogulihe (Fig. 1) are closely related in petrogenesis, owing to their similar geochemical features, including high K$_2$O contents (4–9 wt%), strong enrichment of incompatible elements (Fig. S3) compared to other Cenozoic basalts in eastern China and ocean island basalts, and EM1-like Sr–Nd–Hf isotopic signatures (Zhang et al. 1998; Sun et al. 2014;
Wang et al. 2017). The melt H$_2$O contents of the Xiaogulihe volcanic rocks have been estimated to be 0.36–0.50 wt%, based on Fourier transform infrared spectrometry analyses of H$_2$O contents in clinopyroxene phenocrysts (Chen et al. 2015). Our 4.5 ± 1.2 wt% H$_2$O content estimation of the WEK melts is markedly higher than that of the Xiaogulihe melts. We propose two possible explanations for this difference: (1) the clinopyroxene phenocrysts analyzed by Chen et al. (2015) crystallized after significant degassing; (2) the difference in melt H$_2$O content was inherited from the heterogeneous H$_2$O abundance in the source mantle.

Analyzing the H$_2$O content of clinopyroxene can be a reliable method to retrieve the primary (i.e., pre-eruption) melt H$_2$O content (e.g., Wade et al. 2008; Xia et al. 2013). Application of this method, however, requires that: (1) clinopyroxene had crystallized before significant H$_2$O degassing; and (2) clinopyroxene had not experienced degassing-associated H diffusion. By showing the invariant H$_2$O contents along profiles within clinopyroxene crystals, Chen et al. (2015) demonstrated that the requirement (2) was attained, while the requirement (1) was not fully verified. If the clinopyroxene grains had crystallized during/after magma degassing at shallow depths (e.g., $P <$ 5 kbar), they may record reduced melt H$_2$O contents. To test this possibility, we calculated crystallization pressures for the clinopyroxene grains analyzed by Chen et al. using the Putirka et al. (2003) thermobarometer, and plotted pressure against the corresponding melt H$_2$O content in Fig. 8. The H$_2$O content of the Xiaogulihe melts remains constantly low (~0.3 wt%) as the magma decompressed from 10 kbar to 3 kbar, but shows a notable
rise at $P < 3$ kbar. Considering the high clinopyroxene crystallization pressures (up to 10 kbar), as well as the low and constant melt H$_2$O content during the magma ascending, it is unlikely that degassing occurred prior to the earliest clinopyroxene crystallization. Therefore, we confirm that the clinopyroxene phenocrysts analyzed by Chen et al. (2015) crystallized from undegassed melts, and the low H$_2$O content signature of the Xiaogulihe melts is primary. The absence of deep degassing of the Xiaogulihe magmas is also evidenced by the absence of mantle xenoliths at this volcanic site (Zhang et al. 1998), as the generation and transport of xenoliths is highly dependent on volatile exsolution and bubble nucleation (Lensky et al. 2006). The enhancement of melt H$_2$O content at $P < 3$ kbar can be explained by substantial shallow-level isobaric crystallization under H$_2$O-undersaturated condition (Blundy and Cashman 2008), which is supported by the observed high crystallinity ($\sim$40%) in the Xiaogulihe volcanic rocks (Shao et al. 2009).

Alternatively, the difference in H$_2$O content between the Xiaogulihe and WEK volcanic rocks can be explained by a heterogeneous distribution of H$_2$O in the source mantle, considering the >200 km distance between the two volcanic sites. Although similar in geochemistry, the Xiaogulihe volcanic rocks exhibit more extreme characteristics compared to the WEK basalts, such as the “ultra-high” K$_2$O contents (up to 9.29 wt%, cf. 6.09 wt% for WEK), more enriched large-ion lithophile elements, more fractionated rare earth elements, less radiogenic Pb isotope compositions, and lower $^{143}$Nd/$^{144}$Nd and higher $^{87}$Sr/$^{86}$Sr ratios (Zhang et al. 1998; Sun et al. 2014; Wang et al. 2017). These features indicate a lower melting degree and an isotopically more enriched
source. If the source mantle of the Xiaogulihe volcanic rocks is less hydrous than that of
the WEK basalts, it is reasonable for these rocks to have a lower mantle melting degree at
given $T_p$, and therefore higher $K_2O$ and incompatible element concentrations than the
WEK basalts.

A regional-scale mantle $H_2O$ heterogeneity in eastern China has been recently
revealed; from southeast (close to Pacific subduction zone) to northwest (away from
Pacific subduction zone), the source mantle $H_2O$ contents of the eastern China Cenozoic
basalts tend to decrease from 4700 ppm to 150 ppm (Chen et al. 2017; Xia et al. 2019).
The geochemical characteristics of these basalts are also influenced by increasing
subduction-related fluid activities with decreasing distance to the Pacific plate boundary
(Zhao et al. 2019). This spatial variation of mantle and magma hydration can be most
easily understood as the time-integrated contributions of the wet upwelling fluxes arising
from the MTZ during the subduction and stagnation of the Pacific slab. The Xiaogulihe
volcano is among the westernmost volcanisms in eastern China, ~200 km farther away
from the Pacific trench than WEK, and located far beyond the western edge of the
present-day stagnant Pacific slab (Fig. 1). Therefore, the water content contrast between
the WEK and Xiaogulihe volcanic rocks is consistent with the regional-scale variation
trend. We infer that the source mantle of the WEK and Xiaogulihe potassic volcanic rocks
is heterogeneously hydrated, and the Xiaogulihe volcanic rocks were derived from a less
hydrous domain.
Implications

In most subaerially erupted volcanic rocks, H\textsubscript{2}O dissolved in the melt at depths escapes when the magma ascends to shallower depths and flows towards the surface. Traditionally, melt inclusion analyses and direct measurements of nominally anhydrous minerals (NAMs) can help to constrain the H\textsubscript{2}O content of the melt before eruption. However, melt inclusions that preserve primitive H\textsubscript{2}O contents are not easy to find, and H\textsubscript{2}O in nominally anhydrous minerals is also susceptible to diffusive loss. The method reported in this paper provides a new approach to estimate the primary H\textsubscript{2}O contents of subaerially erupted volcanic rocks despite their having experienced extensive degassing before eruption. This quantitative H\textsubscript{2}O content estimation is useful especially when no direct H\textsubscript{2}O analysis is available.

The Wudalianchi–Erkeshan–Keluo magma is an intraplate magma, which has long been believed to have originated by the dry melting of a lithospheric mantle source. However, our estimation of water contents shows that the WEK magmas with ~4.5 wt% H\textsubscript{2}O have as much water as some arc magmas. This finding is similar to the recent reports on Phanerozoic intraplate large igneous provinces (LIPs) (Xia et al. 2016; Liu et al. 2017; Ivanov et al. 2018), and supports the presence of hydrated deep mantle reservoirs as the sources of these LIPs.

Our method is not restricted to primary melt inclusions or primary NAMs, and therefore, it may be also applicable to some evolved magmatic samples, such as the Martian nakhlite (e.g., Peslier et al. 2019) and chassignite meteorites.
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**Figure captions**

**Figure 1.** Schematic map of the late Cenozoic intraplate volcanic province in Central-East Asia, modified after Wang et al. (2015). The dark gray fields and numbers indicate the locations of the late Cenozoic volcanic fields in Central–East Asia. The thick solid white curves represent plate boundaries. The red dashed curve indicates the western edge of the present-day stagnant Pacific slab (Zhao et al. 2011). Digital topography of
Figure 2. Representative photographs of the WEK basalt samples. (a) Back-scattered electron (BSE) image of a euhedral, zoned clinopyroxene phenocryst from sample HSS5. (b) Microphotograph of sample HSS5, showing glassy features. Clinopyroxene phenocrysts are distributed in the groundmass, which is composed of glass with subordinate clinopyroxene, olivine, and K-feldspar microcrystals. Note the substantial bubbles present in the rock. Cpx denotes clinopyroxene. (c) Field photograph of a surface lava flow of Laoheishan volcano, showing rope-like features, a volcanic bomb, and elongated bubbles. (d) Microphotograph of sample HSS8 showing a euhedral olivine crystal with embayment structure. Ol denotes olivine.

Figure 3. Tests for the thermobarometers. (a) Rhodes’ diagram (Rhodes et al. 1979) for clinopyroxene in the WEK potassic basalts. Mg# = 100×Mg/(Mg+Fe^{2+}), where Mg and Fe^{2+} are in molar fraction. Here the proportion of Fe^{2+} is set to be 100%, following the treatment in experimental calibration (Putirka, 2008). Solid curve: the mean value of the experimental $K_D(\text{Fe–Mg})^{\text{cpx–melt}}$; two dashed curves: 2σ range of the mean experimental $K_D(\text{Fe–Mg})^{\text{cpx–melt}}$; grey field: the range of all experimental $K_D(\text{Fe–Mg})^{\text{cpx–melt}}$ (Putirka 2008). (b) Mg# of clinopyroxene vs. crystallization pressure ($P$) calculated using the clinopyroxene–melt barometer of Putirka et al. (2003). The Mg# value of clinopyroxene

Central-East Asia is from National Oceanic and Atmospheric Administration/National Geophysical Data Center (http://www.ngdc.noaa.gov/mgg/image/).
has a normal distribution and yields an average of \( 81.9 \pm 4.8 \) (2\( \sigma \)), without a decreasing trend as the crystallization pressure decreases. (c) Measured vs. predicted clinopyroxene composition using equations (3.1a), (3.2) and (3.5) of Putirka (1999). All the clinopyroxene grains in equilibrium with their melts are plotted on the 1:1 line within prediction error. DiHd denotes the diopside–hedenbergite component in pyroxene; EnFs denotes the enstatite–ferrosilite component in pyroxene; Jd denotes the jadeite component in pyroxene. (d) Comparison of pressure \((P)\) estimates using the Lee et al. (2009) and Putirka (2008) Si activity barometers for the WEK basalts. Input temperatures are the same in both barometers, which are calculated using the Lee et al. (2009) thermometer with a melt \( \text{H}_2\text{O} \) content of 4.5 wt%. The two barometers yield identical pressure estimates within error.

Figure 4. (a) Pressure–temperature calculation results of the clinopyroxene–melt thermobarometer (Putirka et al. 2003) and the Si activity thermobarometer (Lee et al. 2009) for the WEK basalts. The results of the clinopyroxene–melt thermobarometer (blue circles and the blue field) are linearly fitted and yield \( \frac{dT}{dP} = 8.8 \, ^\circ\text{C}/\text{kbar} \). The Si activity pressures and temperatures are calculated based on different \( \text{H}_2\text{O} \) concentration estimates, which are 0.50 wt% (Chen et al. 2015; red field), 1.4 wt% (Kuritani et al. 2013; green field) and 4.5 wt% (our best estimation value; gray field). Error bars and ellipses are drawn according to Putirka et al. (2003) and Lee et al. (2009). Buffers are constructed for the clinopyroxene–melt thermobarometer and the Si activity thermobarometer by
outlining the corresponding $P$–$T$ points with their error ellipses; see the text for details.

Black dashed curves represent clinopyroxene saturation surfaces of the HSS5 melt with $\text{H}_2\text{O}$ contents of 4 and 5 wt%, calculated using the equation (34) of Putirka (2008). (b) Relationship between the buffer overlapping area/maximal buffer overlapping area (BOA/BOAmax) ratio and the melt $\text{H}_2\text{O}$ content used in the Si activity thermobarometer calculation. The upright dashed line shows the best estimation of the melt $\text{H}_2\text{O}$ content, which is 4.5 wt%.

Figure 5. Estimated vs. experimental (a) melt $\text{H}_2\text{O}$ content, (b) pressure, and (c) temperature, using the experimental data listed in Table 2. Melt $\text{H}_2\text{O}$ contents are estimated using the same method as used for the WEK basalts. Pressures and temperatures are calculated using the Si activity thermobarometer (Lee et al. 2009) with the estimated $\text{H}_2\text{O}$ contents in (a). Red lines show linear fittings of the data points. SEE (standard estimate error) $= \sqrt{\frac{\sum(X_{est} - X_{true})^2}{N}}$, where $X_{est}$ is the estimated value, $X_{true}$ is the true value, $N$ is the number of data.

Figure 6. Modeled $\text{H}_2\text{O}$–$\text{CO}_2$ degassing curves of the WEK magma. Degassing curves are calculated using the model of Duan (2014) and the HSS5 melt composition. The initial state is $\text{H}_2\text{O} = 4.5$ wt% and $\text{CO}_2 = 2.0$ wt% at 13.5 kbar and 1438 K. The red and black curves represent degassing in closed and open system, respectively. The gray curves are $\text{H}_2\text{O}$–$\text{CO}_2$ solubility isobars. The temperature of each isobar is the same as that
of the magma, i.e., determined by $P$/kbar = $-118.0 + 0.113$ $T/°C$. The blue curves are curves of identical vapor composition. The numbers on these curves represent the molar fraction of H$_2$O in the vapor phase.

**Figure 7.** (a) $P$–$T$ path of the WEK magmas extending to higher pressures. Compositions of the low-SiO$_2$ samples are from Zhang et al. (1995) (DZ–6, DZ–3, H–1, MH–4, A–2, H–38); other data points are the same as in Fig. 4a. Silica activity pressures and temperatures are calculated using the estimated 4.5 wt% melt H$_2$O content. Dry and wet ($X_{H2O}^{bulk}$ = 450 ppm) peridotite solidi are plotted using the parameterization of Katz et al. (2003). Mantle potential temperature ($T_p$) is calculated using the model of Putirka (2016), with composition and pressure inputs from the most primary WEK samples. (b) Schematic illustration of the origin of the WEK magmas. Hydrated mantle materials originating from the mantle transition zone (MTZ) crossed the solidus during their upwelling in the convective mantle, and generated small-degree partial melts. The melts stalled at the base of the lithosphere, followed by extraction and rapid magma ascent to the surface. The local Moho depth of 31.3 ± 0.6 km is from Tao et al. (2014); the lithosphere–asthenosphere boundary (LAB) depth of 70–80 km is from Zheng et al. (2011), Li et al. (2012, 2013), and Guo et al. (2014). Depth and pressure are translated assuming a crust average density of 2.7 g/cm$^3$ and a lithospheric mantle average density of 3.3 g/cm$^3$, following Tao et al. (2014).
Figure 8. Pressure–H$_2$O content relation of the Xiaogulihe melts recorded by clinopyroxene crystals. Pressures are calculated using the Putirka et al. (2003) thermobarometer with clinopyroxene and bulk-rock compositions from Chen et al. (2015). Only the clinopyroxene crystals with $K_D$(Fe–Mg)$_{cpx}$–melt between 0.12 and 0.44 were used for $P$ estimation. The melt H$_2$O contents corresponding to the clinopyroxene phenocrysts are from Chen et al. (2015).
Table 1. Example temperature differences at similar pressures calculated using the two thermobarometers.

| H$_2$O (wt%) | Overlapping pressure (kbar) | $P$ (cpx–melt)$^a$ (kbar) | $T$ (cpx–melt)$^a$ (°C) | $P$ (Si activity)$^b$ (kbar) | $T$ (Si activity)$^b$ (°C) | $|\Delta T|$ (°C) |
|-------------|----------------------------|--------------------------|--------------------------|----------------------------|--------------------------|-----------------------------|
| 0           | 8.6–13.5                   | 8.8                      | 1120                     | 8.8                        | 1164                     | 44                          |
|             |                            | 9.1                      | 1121                     | 9.0                        | 1163                     | 42                          |
|             |                            | 9.6                      | 1127                     | 9.6                        | 1171                     | 44                          |
|             |                            | 10.2                     | 1131                     | 10.2                       | 1175                     | 44                          |
|             |                            | 11.3                     | 1140                     | 11.4                       | 1207                     | 67                          |
| 0.5         | 8.8–13.5                   | 8.8                      | 1120                     | 8.8                        | 1170                     | 50                          |
|             |                            | 9.5                      | 1125                     | 9.5                        | 1166                     | 41                          |
|             |                            | 10.3                     | 1134                     | 10.3                       | 1182                     | 48                          |
|             |                            | 10.6                     | 1137                     | 10.6                       | 1184                     | 47                          |
|             |                            | 11.6                     | 1140                     | 11.6                       | 1201                     | 61                          |
| 1.4         | 9.1–13.5                   | 9.1                      | 1151                     | 9.1                        | 1121                     | 30                          |
|             |                            | 9.3                      | 1104                     | 9.3                        | 1124                     | 20                          |
|             |                            | 10.0                     | 1129                     | 10.0                       | 1159                     | 30                          |
|             |                            | 10.8                     | 1135                     | 10.8                       | 1175                     | 40                          |
|             |                            | 11.8                     | 1192                     | 11.9                       | 1146                     | 46                          |
| 3           | 9.6–13.5                   | 9.6                      | 1127                     | 9.6                        | 1139                     | 12                          |
|             |                            | 10.0                     | 1141                     | 10.0                       | 1129                     | 12                          |
|             |                            | 10.5                     | 1147                     | 10.5                       | 1135                     | 12                          |
|             |                            | 11.3                     | 1161                     | 11.3                       | 1140                     | 21                          |
|             |                            | 12.3                     | 1176                     | 12.3                       | 1149                     | 27                          |
| 5           | 10.3–13.5                  | 10.3                     | 1134                     | 10.3                       | 1134                     | 0                           |
|             |                            | 10.6                     | 1137                     | 10.6                       | 1128                     | 9                           |
|             |                            | 11.0                     | 1137                     | 11.0                       | 1132                     | 5                           |
|             |                            | 11.9                     | 1146                     | 11.9                       | 1145                     | 1                           |
|             |                            | 12.8                     | 1154                     | 12.8                       | 1158                     | 4                           |
| 7           | 10.9–13.5                  | 10.9                     | 1136                     | 10.9                       | 1114                     | 22                          |
|             |                            | 11.3                     | 1140                     | 11.2                       | 1116                     | 24                          |
|             |                            | 11.6                     | 1140                     | 11.6                       | 1120                     | 20                          |
|             |                            | 12.4                     | 1149                     | 12.4                       | 1125                     | 24                          |
|             |                            | 13.5                     | 1162                     | 13.3                       | 1143                     | 19                          |
| 9           | 11.5–13.5                  | 11.6                     | 1140                     | 11.5                       | 1105                     | 35                          |
|             |                            | 11.9                     | 1146                     | 11.9                       | 1107                     | 39                          |
|             |                            | 12.3                     | 1149                     | 12.2                       | 1110                     | 39                          |
|             |                            | 12.4                     | 1149                     | 12.4                       | 1111                     | 38                          |
Pressures and temperatures are calculated using the clinopyroxene–melt thermobarometer of Putirka et al. (2003).

Pressures and temperatures are calculated using the Si activity thermobarometer of Lee et al. (2009).

$|\Delta T| = |T(\text{cpx–melt}) - T(\text{Si activity})|$. Note $|\Delta T|$ is minimized at $\text{H}_2\text{O}$ content of 5 wt%. 

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Table 2. Summary of the experimental data used for testing the water content estimation method.

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<th>T (°C)</th>
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<th>H$_2$O$^\text{melt}$ error$^b$ (wt%)</th>
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\(a\) liq = liquid, ol = olivine, cpx = clinopyroxene, opx = orthopyroxene, plag = plagioclase, spn = spinel, grt = garnet, amph = amphibole, ilm = ilmenite.

\(b\) n.r., not reported.
H₂O content when BOA is maximized.

Pressures and temperatures are calculated using the Si activity thermobarometer (Lee et al. 2009) with the estimated melt H₂O contents.
Table 3. Thermal expansion coefficient ($\alpha$), specific heat capacity ($c_p$), and density ($\rho$) data of basaltic melts, water, and carbon dioxide at 1400 K and 10 kbar.

<table>
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<tr>
<th></th>
<th>$\alpha$ (10^{-4} K^{-1})</th>
<th>$c_p$ [10^3 J/(kg·K)]</th>
<th>$\rho$ (10^3 kg/m^3)</th>
<th>$(\partial T/\partial P)_S$ (°C/kbar)</th>
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<td>Volatile-free HSS5 melt$^a$</td>
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$^a$ Calculated using the partial molar thermodynamic properties from Lesher and Spera (2015); the melt composition is from Chu et al. (2013).

$^b$ From McKenzie and Bickle (1988).

$^c$ Calculated using the model of Verma (2003).

$^d$ From Bottinga and Richet (1981).

$^e$ $(\partial T/\partial P)_S = T\alpha/(\rho c_p)$, where $T$ is the temperature (1400 K).
Figure 1

1-Sovetskaya Gavan 7-Jining-Hannuoba
2-Shikoto-Sufan 8-Abaga
3-Changbaishan 9-Tokin Stanovik
4-Jingpohu-Mudanjiang 10-Udokan
5-Wudalianchi-Erkeshan-Kelu (WEK) 11-Vitim
6-Chifeng 12-Southern Baikal
7-Jining-Hannuoba 13-Southern Hangai

Legend:
- WEK
- Pacific Plate
- China
- Mongolia
- Russia
- Sea of Okhotsk
- Japan Sea
- East China Sea
- Xiaogulihe
Figure 2
Figure 3

![Diagram of Mg# (cpx) vs. P(kbar) with Phenocryst and Groundmass data points.](image)

Mg# = 81.9 ± 4.8

![Diagram showing DiHd, EnFs, Jd molar fractions vs. Measured molar fractions.](image)

![Diagram showing Measured molar fractions vs. P(kbar) with 1:1 line and error bars.](image)
Figure 4

(a) Increasing H$_2$O buffer for cpx-melt thermobarometer-determined range. Overlapping range for Si activity thermobarometer-determined range.

(b) BOA / BOA$_{\text{max}}$ vs. H$_2$O (wt%) for various H$_2$O concentrations:
- H$_2$O = 0.50 wt%
- H$_2$O = 1.4 wt%
- H$_2$O = 4.5 wt%
Figure 5

(a) Estimated vs. Measured H₂O (wt%)
- R² = 0.49
- SEE = 1.2 wt%
- Slope = 0.61
- Intercept = 1.4 wt%
- N = 21

(b) Estimated P (kbar) vs. Experimental P (kbar)
- R² = 0.90
- SEE = 1.7 kbar
- Slope = 0.95
- Intercept = 1.3 kbar
- N = 21

(c) Estimated T (°C) vs. Experimental T (°C)
- R² = 0.83
- SEE = 47 °C
- Slope = 0.58
- Intercept = 518 °C
- N = 21
Figure 6
Figure 7

- Crust
- SCLM
- LAB

- Moho
- Dry solidus
- Wet solidus

- $T_p = 1372 \pm 30 \degree C$

- WEK volcanos
- Magma ascending
- Melt ponding?
- Partial melting
- Wet upwelling from MTZ
Figure 8

Crystallization?