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## Geo-fO<sub>2</sub>: Integrated Software for Analysis of Magmatic Oxygen Fugacity

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## TECHNICAL REPORTS: METHODS

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### Key Points:

- Oxygen fugacity ( $fO_2$ ) is a fundamental thermodynamic property that governs the redox potential in solid Earth systems
- Specialized software, Geo- $fO_2$ , was developed for analysis of magmatic  $fO_2$
- With user-friendly interfaces, Geo- $fO_2$  is easy to input files, output data in Excel files, and plot results as binary diagrams

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- Supporting Information S1
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## Geo- $fO_2$ : Integrated Software for Analysis of Magmatic Oxygen Fugacity

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**Abstract** Oxygen fugacity ( $fO_2$ ) is a fundamental thermodynamic property governing redox potential in solid Earth systems. Analysis of magmatic  $fO_2$  aids our understanding of the valence state and solubility of multivalent elements during magma evolution. Specialized software, Geo- $fO_2$ , was developed for calculating magmatic  $fO_2$  on the basis of oxybarometers and thermobarometers for common minerals (amphibole, zircon, and biotite) in intermediate-silicic magmas. With user-friendly interfaces, it is easy to input files (.csv or Excel files), output data in Excel files, and plot results as binary diagrams that can be saved as vector graphics and modified using image-processing software.

### 1. Introduction

Oxygen fugacity ( $fO_2$ ) is defined as the partial pressure of oxygen within a system (e.g., Carmichael, 1991; Frost, 1991; Lee et al., 2005) and is a fundamental thermodynamic property governing redox potential in solid Earth systems. In particular, during magma evolution the  $fO_2$  controls valence states of multivalent elements (e.g., Fe, Cu, Au, V, S, and C), which in turn controls their crystal/melt partitioning (e.g., Brounce et al., 2014; Canil, 2002) and solubility in silicate magmas (e.g., Carmichael, 1991; Evans & Tomkins, 2011; Rowe et al., 2009). This is particularly crucial for ore mineralization in magmatic-hydrothermal systems (e.g., porphyry-type deposits; Jugo, 2009; Richards, 2015; Sillitoe, 2010; Simon & Ripley, 2011; Yang et al., 2016; Zajacz et al., 2011) and speciation of volatiles during magma degassing (e.g., Burgisser & Scaillet, 2007; Clémente et al., 2004; Iacono-Marziano et al., 2012; Jugo et al., 2005; Mathez, 1984; Moretti & Ottonello, 2005; Pawley et al., 1992).

Two early models for the calculation of magmatic  $fO_2$  involved bulk  $Fe^{3+}/Fe^{2+}$  (or  $Fe^{3+}/\Sigma Fe$ ) ratios (e.g., Kennedy, 1948; Kilinc et al., 1983; Kress & Carmichael, 1991; Sack et al., 1981) and the Fe-Ti oxide oxybarometer (e.g., Andersen & Lindsley, 1985; Buddington & Lindsley, 1964; Carmichael, 1966; Ghiorso & Sack, 1991). Corresponding programs include QUILF (Andersen et al., 1993), MELTS (Ghiorso et al., 2002; Ghiorso & Sack, 1995; Smith & Asimow, 2005), ILMAT (Lepage, 2003), and Petrolog3 (Danyushevsky & Plechov, 2011). However, bulk  $Fe^{3+}/Fe^{2+}$  ratios in rocks are highly susceptible to alteration by weathering, hydrothermal modification, and degassing and also susceptible to early fractional crystallization of mafic minerals (e.g., olivine; Cottrell & Kelley, 2011). The Fe-Ti oxide oxybarometer is limited to magmas that precipitate both ilmenite and magnetite solid-solution during cooling. Additionally, Fe-Ti oxides tend to reequilibrate at subsolidus temperatures during slow cooling or due to hydrothermal alteration (Venezky & Rutherford, 1999). Consequently, the oxybarometer is typically applied to volcanic rather than intrusive systems.

Recently, some new mineral oxybarometers have been calibrated on the basis of the composition of relatively stable and common minerals, which are often found in intermediate-silicic magmas, such as zircon (Ballard et al., 2002; Burnham & Berry, 2012; Smythe & Brennan, 2016; Trail et al., 2011, 2012, 2015) and amphibole (Ridolfi et al., 2010; Ridolfi & Renzulli, 2012). These oxybarometers, plus previously calibrated oxybarometers for other minerals (e.g., biotite; Wones, 1972, 1981; Wones & Eugster, 1965), make it possible to track initial magmatic  $fO_2$  and its subsequent variations (e.g., Li et al., 2019). A few programs developed for individual minerals are available for simple estimations of magmatic  $fO_2$  (e.g., Ridolfi et al., 2010; Yavuz, 2003a, 2003b; Yavuz & Öztaş, 1997); however, specialized software integrating previously and recently calibrated oxybarometers that can systematically calculate and visualize magmatic  $fO_2$  is lacking.

In this study, we developed user-friendly interfaces for the first version of integrated software, “Geo- $fO_2$ ,” written in Python (van Rossum & Drake, 1995, 2011). Geo- $fO_2$  includes oxybarometers and thermobarometers of zircon (Ferry & Watson, 2007; Miller et al., 2003; Trail et al., 2011; Watson & Harrison, 1983), amphibole (Ridolfi et al., 2010; Schmidt, 1992), and biotite (Henry et al., 2005; Uchida et al., 2007; Wones, 1972). It is designed to (1) calculate cations in minerals; (2) calculate thermodynamic parameters of magma (e.g.,  $fO_2$ , temperature, and pressure) during magma ascent and fractional crystallization; and (3) visualize calculated results through a plotting interface.

## 2. Methods

### 2.1. Amphibole Oxybarometer, Thermobarometer, and Hygrometer

Amphibole is an important mineral in hydrous magmas and is stable across a wide  $P$ - $T$  range (700–1100 °C; 0.1–25 kbar; Allen & Boettcher, 1978; Eggler, 1972; Nandedkar et al., 2014). Based on electron microprobe analysis (EMPA) data of amphibole, Ridolfi et al. (2010) produced the  $\Delta NNO$ - $Mg^*$  oxybarometer ( $\Delta NNO$  is the deviation of  $\log fO_2$  from the Ni-NiO buffer [NNO; O'Neill & Pownceby, 1993]), Si\*-sensitive thermometer,  $Al_T$ -sensitive barometer, and  $^{VI}Al^*$ -sensitive hygrometer to estimate  $fO_2$ , temperature, pressure, and  $H_2O$  contents of magma, respectively, from which amphibole crystallizes, as described by the following formulae:

$$\Delta NNO = (1.644 \times Mg^*) - 4.01 \quad (\sigma_{est} = \pm 0.22 \text{ log unit}), \quad (1)$$

where  $Mg^* = Mg + (Si/47) - (Al^{VI}/9) - (1.3 \times Ti^{VI}) + (Fe^{3+}/3.7) + (Fe^{2+}/5.2) - ({}^B Ca/20) - ({}^A Na/2.8) + ((1 - {}^A Na - {}^A K)/9.5)$ ; Mg, Si,  $Al^{VI}$ ,  $Ti^{VI}$ ,  $Fe^{3+}$ , and  $Fe^{2+}$  represent the number of atoms of each per formula unit based on 13 cations;  $Al^{VI}$  and  $Ti^{VI}$  are the numbers of Al and Ti atoms in octahedral sites;  ${}^A Na$  and  ${}^A K$  are the Na and K contents of A sites; and  ${}^B Ca$  is the Ca content of B sites. The  $\sigma_{est}$  represents the standard error of the calibration (Ridolfi et al., 2010); the same below.

$$T \text{ (}^\circ\text{C)} = (-151.487 \times Si^*) + 2041 \quad (\sigma_{est} = \pm 22 \text{ }^\circ\text{C}), \quad (2)$$

where  $Si^* = Si + (Al^{IV}/15) - (2 \times Ti^{IV}) - (Al^{VI}/2) - (Ti^{VI}/1.8) + (Fe^{3+}/9) + (Fe^{2+}/3.3) + (Mg/26) + ({}^B Ca/5) + ({}^B Na/1.3) - ({}^A Na/15) + ((1 - {}^A Na - {}^A K)/2.3)$ ;  $Al^{IV}$  and  $Ti^{IV}$  are the numbers of Al and Ti atoms in tetrahedral sites;  ${}^B Na$  is the Na content of B sites.

$$P \text{ (kbar)} = 0.19209 \times e^{(1.438 Al_T)} \quad (\sigma_{est} = \pm 0.54 \text{ kbar}), \quad (3)$$

where  $Al_T$  is the total number of Al atoms per amphibole unit formula.

$$H_2O \text{ (wt.}\%) = (5.215 \times {}^{VI}Al^*) + 12.28 \quad (\sigma_{est} = \pm 0.4 \text{ wt.}\%), \quad (4)$$

where  ${}^{VI}Al^* = Al^{VI} + (Al^{IV}/13.9) - ((Si + Ti^{VI})/5) - ({}^C Fe^{2+}/3) - (Mg/1.7) + (({}^B Ca + 1 - {}^A Na - {}^A K)/1.2) + ({}^A Na/2.7) - (1.56 \times {}^A K) - (Fe\#/1.6)$ ;  ${}^C Fe^{2+}$  is the  $Fe^{2+}$  content of C sites;  $Fe\# = Fe^{3+}/(Fe^{3+} + Fe^{2+} + Mg + Mn)$ .

The classical Al-in-amphibole barometer of Schmidt (1992) is also provided:

$$P \text{ (kbar)} = -3.01 + (4.76 \times Al_T) \quad (\sigma_{est} = \pm 0.6 \text{ kbar}), \quad (5)$$

where  $Al_T$  is the total number of Al atoms per amphibole unit formula.

### 2.2. Zircon Oxybarometer, Thermometer, and $Ce^{4+}/Ce^{3+}$ Ratios

Zircon is an exceptionally durable mineral that retains primary chemistry for most elements and isotopes from the time of its igneous crystallization (Cherniak et al., 1997). Zircon saturation temperature can be obtained by using the Zr saturation thermometer of Watson and Harrison (1983):

$$\ln D_{Zr}^{zircon/melt} = -3.8 - (0.85 \times (M - 1)) + (12,900 / (T + 273.15)), \quad (6)$$

where  $D_{Zr}^{zircon/melt}$  is the Zr concentration ratio between zircon and melt,  $T$  is temperature (°C), and  $M = (Na + K + 2Ca)/(Al \times Si)$  is the cation ratio of the bulk components. If the Zr contents of zircons are unknown, an approximate content of 496,000 ppm is used for magmatic zircons (Miller et al., 2003).

Another revised Ti-in-zircon thermometer (Ferry & Watson, 2007) allows calculation of zircon crystallization temperature (°C) using the Ti content (ppm) of zircon ( $Ti_{\text{zircon}}$ ) and activities of  $SiO_2$  ( $a_{SiO_2}$ ) and  $TiO_2$  ( $a_{TiO_2}$ ) in host melt:

$$\log Ti_{\text{zircon}} = (5.711 \pm 0.072) - (4,800 \pm 86) / (T + 273.15) - \log a_{SiO_2} + \log a_{TiO_2}. \quad (7)$$

For quartz-saturated melts,  $a_{SiO_2}$  is set to 1.0, and  $a_{TiO_2}$  can be estimated using the activity model of Ghiorso and Gualda (2013). In Geo-fO<sub>2</sub>, a manual input box allows the user to input appropriate values of  $a_{SiO_2}$  and  $a_{TiO_2}$  as described in section 3.

Trail et al. (2011) provided a zircon oxybarometer for determining the redox state of magmas based on the Ce anomaly in zircon. The Ce anomaly is defined as the degree to which the calculated Ce partition coefficient differs from that expected based on partition coefficients of its neighboring elements, La and Pr. It is expressed as  $(Ce/Ce^*)_D$

$$(Ce/Ce^*)_D = D_{Ce}^{\text{zircon/melt}} / \left( D_{La}^{\text{zircon/melt}} \times D_{Pr}^{\text{zircon/melt}} \right)^{1/2}, \quad (8)$$

$$\ln (Ce/Ce^*)_D = (0.1156 \pm 0.0050 \times \ln fO_2) + ((13,860 \pm 708) / (T + 273.15)) - (6.15 \pm 0.484), \quad (9)$$

where  $D_{Ce}^{\text{zircon/melt}}$ ,  $D_{La}^{\text{zircon/melt}}$ , and  $D_{Pr}^{\text{zircon/melt}}$  are partition coefficients of Ce, La, and Pr between zircon and melt, respectively, and  $T$  is temperature (°C). If components of the melt are not available, bulk components of host rock are allowed to be used as an alternative.

However, the accurate determination of Ce anomalies based on La and Pr contents is often problematic due to the low La and Pr concentrations in zircon (e.g., Dilles et al., 2015; Qiu et al., 2013; Trail et al., 2012; Wang et al., 2014). Studies of natural zircon/melt partitioning have suggested that it can be reasonably assumed that  $(Ce/Ce^*)_D \approx (Ce/Ce^*)_{CHUR}$  (e.g., Hinton & Upton, 1991; Sano et al., 2002; Thomas et al., 2002). However, Ce anomaly in the melt during zircon crystallization may have been influenced by some magmatic processes, that is, calculated  $(Ce/Ce^*)_{CHUR}$  values may be overestimated under oxidized conditions due to fractional crystallization (e.g., monazite; Skora & Blundy, 2010; Stepanov et al., 2012) or contamination (Elderfield et al., 1981; Trail et al., 2012). As an alternative, the lattice-strain model (LSM; Blundy & Wood, 1994) may be used to estimate zircon Ce anomalies (expressed as  $(Ce/Ce^*)_{LSM}$ ) using more enriched rare Earth elements (REEs; e.g., Nd, Sm, and Gd–Lu; Qiu et al., 2013; Trail et al., 2012) with better statistics (Burnham & Berry, 2012; Smythe & Brenan, 2016; Zou et al., 2019).  $(Ce/Ce^*)_D$  was therefore set at  $(Ce/Ce^*)_D = (Ce/Ce^*)_{LSM}$  for Ce anomalies in this study. Specifically, the partition coefficient of cation  $i$  between zircon and melt is related to the lattice-strain energy created by substituting a cation with an ionic radius ( $r_i$ ) different to the optimal value for that site ( $r_0$ ; Blundy & Wood, 1994). The corresponding expression is

$$\ln D_i = \ln D_0 - (4\pi \times E \times N_A \times (r_i/3 + r_0/6) \times (r_i - r_0)^2) / (R \times (T + 273.15)), \quad (10)$$

where  $D_0$  is the strain-compensated partition coefficient,  $E$  is Young's modulus,  $N_A$  is Avogadro's number,  $R$  is the gas constant, and  $T$  is temperature (°C). Plotting  $\ln D_i$  versus the term  $(r_i/3 + r_0/6) \times (r_i - r_0)^2$  yields a linear relationship for isoivalent series of cations. If the ionic radii of  $Ce^{4+}$  and  $Ce^{3+}$  are known, their partition coefficients can be determined by interpolation (see also in Smythe & Brenan, 2016). The value of  $D_{Ce}^{\text{zircon/melt}}$  lies between the partition coefficients of the two valence-state end-members ( $Ce^{4+}$  and  $Ce^{3+}$ ), and the magmatic  $fO_2$  can be determined by combination of equations (8) and (9). REE ionic radii were taken from Shannon (1976).

Zircon  $Ce^{4+}/Ce^{3+}$  ratios (Ballard et al., 2002) offer another method for estimating magma redox states. The ionic radius of  $Ce^{4+}$  (0.87 Å) is similar to that of  $Zr^{4+}$  (0.72 Å) and smaller than  $Ce^{3+}$  (1.01 Å; Shannon,

1976), so  $Ce^{4+}$  may substitute for  $Zr^{4+}$  in zircons. Under oxidized conditions, Ce occurs mainly as  $Ce^{4+}$ , and high  $Ce^{4+}/Ce^{3+}$  ratios thus indicate oxidized conditions:

$$Ce^{4+}/Ce^{3+} = \left( Ce_{melt} - Ce_{zircon} / D_{Ce^{3+}}^{zircon/melt} \right) / \left( Ce_{zircon} / D_{Ce^{4+}}^{zircon/melt} - Ce_{melt} \right), \quad (11)$$

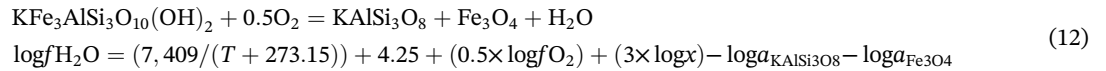
$$Ce^{4+} = \left( Ce_{melt} - Ce_{zircon} / D_{Ce^{3+}}^{zircon/melt} \right) / \left( 1 / D_{Ce^{4+}}^{zircon/melt} - 1 / D_{Ce^{3+}}^{zircon/melt} \right), \quad (11.1)$$

$$Ce^{3+} = Ce_{zircon} - \left( Ce_{melt} - Ce_{zircon} / D_{Ce^{3+}}^{zircon/melt} \right) / \left( 1 / D_{Ce^{4+}}^{zircon/melt} - 1 / D_{Ce^{3+}}^{zircon/melt} \right), \quad (11.2)$$

where  $Ce_{zircon}$  and  $Ce_{melt}$  represent Ce concentrations in zircon and melt and  $D_{Ce^{4+}}^{zircon/melt}$  and  $D_{Ce^{3+}}^{zircon/melt}$  represent partition coefficients of  $Ce^{4+}$  and  $Ce^{3+}$  between zircon and melt. The  $Ce^{4+}/Ce^{3+}$  ratio is obtained by calculating  $Ce^{4+}$  and  $Ce^{3+}$  separately using the LSM.

### 2.3. Biotite Oxybarometer and Thermobarometer

Biotite is commonly present in igneous rocks and reacts sensitively to changes in physicochemical conditions such as temperature, pressure, halogen fugacity,  $fO_2$ , and magma composition (Speer, 1984). Although biotite tends to reequilibrate at subsolidus temperatures or due to hydrothermal alteration (e.g., Li et al., 2019), equilibrium assemblage biotite-magnetite-sanidine (K-feldspar) can be used to estimate magmatic  $fO_2$  during crystallization according to the equilibrium reaction and empirical equation (Wones, 1972):



where  $f_{H_2O}$  is water fugacity,  $T$  is temperature ( $^{\circ}C$ ),  $x$  is the mole fraction of  $Fe^{2+}$  in the octahedral site of biotite, and  $a$  is the activity of the subscripted components indicated. Waldbaum and Thompson (1969) have shown that alkali feldspar solid solutions are distinctly non-ideal. Here  $a_{KAlSi_3O_8}$  is calculated from the ternary feldspar (anorthite-albite-orthoclase) model of Elkins and Grove (1990). For the calculation of  $f_{H_2O}$ , if either the partial pressure  $P_{H_2O}$ , the fugacity coefficient  $\gamma_{H_2O}$ , or the mole fraction in the fluid  $X_{H_2O}^{fluid}$  is known, the remaining two parameters for  $H_2O$  can be solved by using the relationships:

$$P_{H_2O} = f_{H_2O} / \gamma_{H_2O} = (f_{H_2O}^{pure} \times X_{H_2O}^{fluid}) / \gamma_{H_2O}, \quad (13)$$

where  $f_{H_2O}^{pure}$  is the fugacity of the pure  $H_2O$ . The  $\gamma_{H_2O}$  can be calculated by using the modified Redlich-Kwong equation (Holloway & Blank, 1994), given critical temperature, critical pressure, and the acentric factor  $\omega$  (Iacovino, 2014; Prausnitz et al., 1998). Detailed calculation process for  $\gamma_{H_2O}$  can be found in the Appendix of Holloway and Blank (1994).

The solid-solution model of Woodland and Wood (1994) is used to calculate  $a_{Fe_3O_4}$ :

$$a_{Fe_3O_4} = (X_{mag})^2 \times \gamma_{mag}, \quad (14)$$

$$R \times T \times \ln(\gamma_{mag}) = (10,580 + 63,060 \times X_{mag}) \times (1 - X_{mag})^2, \quad (15)$$

where  $R$  is the gas constant,  $X_{mag}$  is the mole fraction of the magnetite endmember in the magnetite-ulvöspinel solid solution (Carmichael, 1966), and  $\gamma_{mag}$  is the activity coefficient of magnetite.  $X_{mag}$  is calculated using the similar algorithm as in the QUILF program (Andersen et al., 1993). The temperature of biotite crystallization can be obtained by the Ti-in-biotite geothermometer (see below). By substituting  $X_{mag}$  and temperature into equation (15),  $\gamma_{mag}$  can be calculated. Combination of equations (14) and (15) gives the value of  $a_{Fe_3O_4}$ .

Ti-in-biotite geothermometer is from Henry et al. (2005):

$$T (^{\circ}\text{C}) = \left( \left( \ln \text{Ti} + 2.3594 + 1.7283 \times (X_{\text{Mg}})^3 \right) / (4.6482 \times 10^{-9}) \right)^{0.333}. \quad (16)$$

This empirical equation is strictly valid only for  $X_{\text{Mg}} = \text{Mg}/(\text{Mg} + \text{Fe}) = 0.275\text{--}1.000$ ,  $\text{Ti} = 0.04\text{--}0.60$  atoms of each per formula unit calculated on the basis of 22 oxygen atoms, and  $T = 480\text{--}800^{\circ}\text{C}$ . Standard deviation of the Ti-in-biotite geothermometer is estimated to be  $\pm 24^{\circ}\text{C}$  at temperatures of  $480\text{--}600^{\circ}\text{C}$ ,  $\pm 23^{\circ}\text{C}$  at  $600\text{--}700^{\circ}\text{C}$ , and  $\pm 12^{\circ}\text{C}$  at  $700\text{--}800^{\circ}\text{C}$  (Henry et al., 2005). Calibration of this geothermometer was based on compositions of biotite in metamorphic rocks. To check its applicability to igneous rocks, experimental data for magmatic biotites (Andújar et al., 2008; Andújar & Scaillet, 2012; Fabbrizio et al., 2006; Fabbrizio & Carroll, 2008; Mutch et al., 2016; Nandedkar et al., 2014) were used to calculate crystallization temperature using equation (16). Differences between calculated and experimentally measured temperatures were in the range of  $-26^{\circ}\text{C}$  to  $+65^{\circ}\text{C}$  (see supporting information Table S1). In addition, a large number of published biotite data collected from intermediate-silicic intrusions worldwide (e.g., Helmy et al., 2004; Hossain & Tsunogae, 2014; Sarjoughian et al., 2012; Wang et al., 2014) were used to check the applicability of this geothermometer in igneous systems. In the same intrusion, calculated crystallization temperatures of biotites (magmatic Mg-biotites) are  $5^{\circ}\text{C}$  to  $228^{\circ}\text{C}$  lower than crystallization temperatures of amphiboles (Mg-amphibole and Tschermakites; supporting information Table S1), which match the magmatic crystallization sequence determined by petrographic observations of each intrusion.

The pressure of magmatic biotite crystallization may be estimated using the  $^{\text{T}}\text{Al}$ -geobarometer (Uchida et al., 2007):

$$P (\text{kbar}) = 3.03 \times \text{Al}_{\text{T}} - 6.53 \quad (\sigma_{\text{est}} = \pm 0.33 \text{ kbar}), \quad (17)$$

where  $\text{Al}_{\text{T}}$  is the total number of Al atoms in biotite calculated on the basis of 22 oxygens.

### 3. Software Description

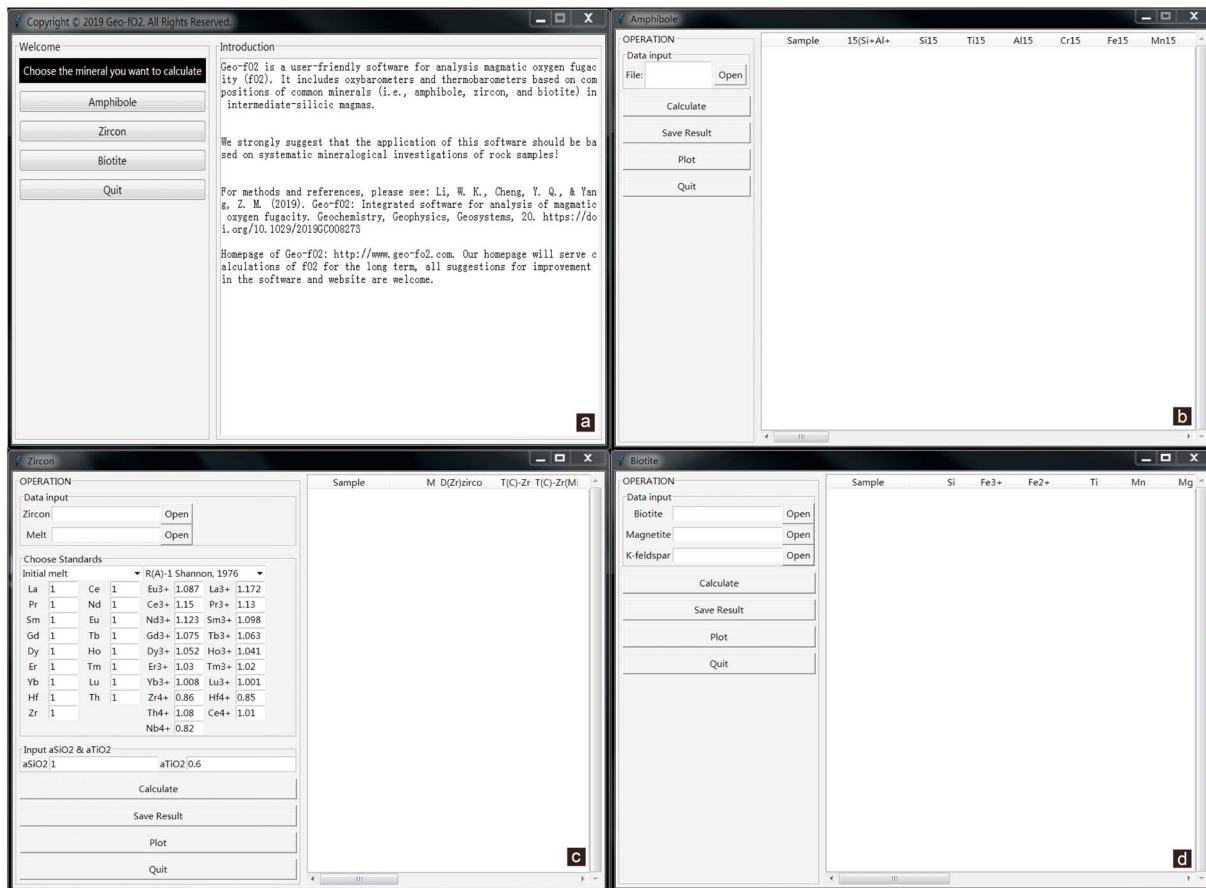
Geo- $f\text{O}_2$  is packaged as an installation-free .exe file that can run in Windows platforms. Under Mac OS platforms, the user can also use Geo- $f\text{O}_2$  through an application such as Wine or Winebottler. Control panel interfaces consist of one main interface and three mineral subinterfaces (Figure 1). The main interface has four buttons, “Amphibole,” “Zircon,” “Biotite,” and “Quit” (Figure 1a). Clicking a mineral button brings up a corresponding mineral subinterface (Figures 1b–1d). The user is able to exit the software by clicking “Quit” or the “x” button in the upper right corner of the main interface. The mineral subinterfaces (Figures 1b–1d) are divided into two parts, which are the left OPERATION panel and right preview window showing calculated results. Main operations in the left panel include “Data input,” “Calculate,” “Save Result,” “Plot,” and “Quit.” The user can return to the main interface by clicking the “Quit” or “x” button.

#### 3.1. Data Input

In the Data input subpanel, the user loads the data file from the desired folder. The user may view and select the input file (i.e., .csv, .xlsx, or .xls files) by clicking the “Open” button. The first column of the input file must contain the names of the oxides and/or trace elements. After selection of the input file, the program automatically extracts and rearranges data. Although this is automatic, we suggest the user uses the recommended model input Excel tables as the input files in order to avoid calculation errors caused by special characters (see supporting information tables: Table S2—model input Excel table of amphibole; Table S3—model input Excel table of zircon; Table S4—model input Excel table of host melt (or host rock) components of corresponding zircon grains used in Table S3, only one set of melt components (or bulk components) is allowed to be used per calculation; Tables S5, S6, and S7—model input Excel tables of biotite, K-feldspar, and magnetite, respectively).

#### 3.2. Calculation

Calculation is executed by clicking the “Calculate” button in the three mineral subinterfaces (Figures 1b–1d).

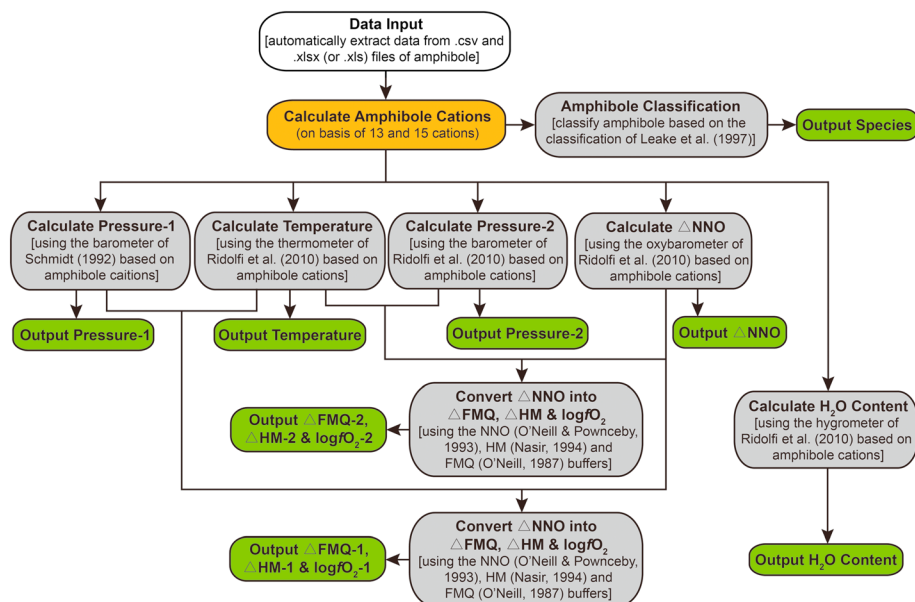


**Figure 1.** The main interface (a) and three mineral subinterfaces (b–d) of Geo- $fO_2$  illustrating major features of this software.

### 3.2.1. Amphibole

Calculations for amphibole use the EMPA data, with a process as shown in Figure 2. Mineral formulae for amphibole were calculated following the International Mineralogical Association recommendation for calcic amphiboles, where  $Fe^{3+}/Fe^{2+}$  ratios are determined by charge balance after adjusting total tetrahedral (Si, Al, and Ti) plus octahedral (Al, Ti, Cr, Fe, Mn, and Mg) cations to 13 (Leake et al., 1997; Ridolfi et al., 2010). Because the 13 cation calculation determines the minimum alkali content in A site (i.e.,  $^A(Na + K)$ ) and  $Al^{VI}$ , and the maximum  $Fe^{3+}$ , calculation on the basis of 15 cations is also provided to get the maximum  $^A(Na + K)$  and  $Al^{VI}$ , and the minimum  $Fe^{3+}$  (Ridolfi et al., 2010). The calculated cation data are then used in amphibole classifications according to the principle of Leake et al. (1997, Figure 3 therein) and following calculations of different parameters.

Another four parallel calculations (Figure 2) based on calculated amphibole cation data include  $P$ ,  $T$ ,  $\Delta NNO$  value, and  $H_2O$  content. Calculations of  $Si^*$ -sensitive thermometer and  $\Delta NNO-Mg^*$  oxybarometer are very stable within the conditions of 550–1120 °C and  $-1 \leq \Delta NNO \leq +5$  (Ridolfi et al., 2010). The calculated  $\Delta NNO$  is converted into  $\Delta FMQ$  and  $\Delta HM$  values ( $\Delta FMQ$  and  $\Delta HM$  are the deviation of  $\log fO_2$  from the fayalite-magnetite-quartz buffer [FMQ; O'Neill, 1987] and the hematite-magnetite buffer [HM; Nasir, 1994]), based on two sets of combined values of calculated temperatures and pressures (Figure 2). The program also translates  $\Delta NNO$  into absolute  $\log fO_2$ . Although calculated standard error of  $Al_T$ -sensitive barometer is 0.54 kbar, it strongly decreases to 0.39 kbar at  $P < 4.5$  kbar, where the average relative error is  $\pm 14\%$  (Ridolfi et al., 2010). At 1 GPa, the relative error can be as high as 33%, but it decreases to 8% for the amphiboles at the physical-chemical stability boundaries (Ridolfi et al., 2010). The relative error of this barometer is  $< 11\%$  near the  $P$ - $T$  stability curve, whereas for crystal-rich (i.e., porphyritic index  $> 35\%$ ) and lower- $T$  magmas, the relative error increases up to 24%, consistent with depth relative error of  $\pm 0.4$  km at



**Figure 2.** Flowcharts summarizing the basic workflow for calculating mineral cations and thermodynamic parameters on the basis of amphibole. White box represents data input and extract process; orange box represents mineral cations calculation process based on mineral formulae; gray boxes are the calculation process of  $T$ ,  $P$ , and  $fO_2$ ; green boxes represent the output process of calculated  $T$ ,  $P$ , and  $fO_2$  data. NNO = Ni–NiO buffer; FMQ = fayalite-magnetite-quartz buffer; HM = hematite-magnetite buffer.

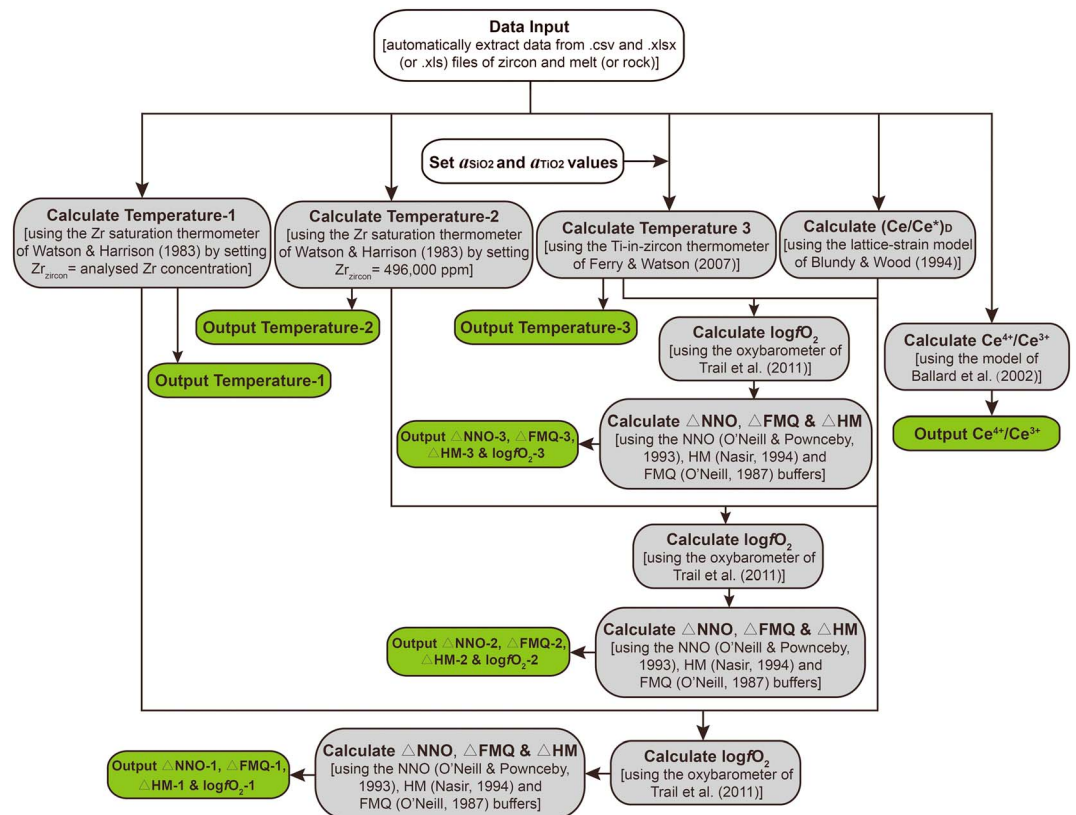
0.9 kbar (~3.4 km) and  $\pm 7.9$  km at 8.0 kbar (~30 km). As a result, we strongly suggest using this barometer with amphibole compositions having  $Al^V/Al_T \leq 0.21$  and  $Mg/(Mg + Fe^{2+}) > 0.5$  (Ridolfi et al., 2010). The user may preview all results in the right preview window for each mineral subinterface (Figures 1b–1d).

### 3.2.2. Zircon

Zircon calculations are based on elemental contents of zircon (i.e., trace element) and host rock (i.e., major and trace elements). Calculation processes are shown in Figure 3. By default, Geo- $fO_2$  only allows the user to calculate zircon data from one rock sample at one time because Geo- $fO_2$  has no automatic matching function. For example, if the user has two groups of zircon trace element data from two different rock samples, Samples 1 and 2,  $fO_2$  values of the two groups should be calculated separately, using the corresponding combination of zircons and host rock. More specifically, by inputting bulk components of Sample 1 and trace element data of zircons yielded in rock Sample 1, the user can obtain  $fO_2$  values of Sample 1. If the user wants to get  $fO_2$  values of Sample 2, the user has to repeat above calculation procedure. In this case, the user therefore cannot get two groups of  $fO_2$  values through one calculation.

The Zr saturation temperature is calculated from the partitioning of Zr between zircon and host melt. The program gives two sets of Zr saturation temperature based on two thermometers (Miller et al., 2003; Watson & Harrison, 1983). Before calculation of temperature by the Ti-in-zircon thermometer, the program requires the user to manually set  $a_{SiO_2}$  and  $a_{TiO_2}$  values through input boxes in the “Input  $a_{SiO_2}$  &  $a_{TiO_2}$ ” subpanel (Figure 1c). The initial values are set to 1.0 and 0.6, respectively (0.6 is almost the minimum in silicic melts; Ferry & Watson, 2007; Hayden & Watson, 2007; Watson et al., 2006). Therefore, three temperatures (two Zr saturation and one Ti-in-zircon temperatures) are provided in the final output Excel table based on one set of zircon-melt data (Figure 3).

The zircon subinterface has an extra subpanel, “Choose Standards,” which serves the  $(Ce/Ce^*)_D$  calculation. When the input file of melt components is selected, the program automatically extracts REE, Hf, Th, and Zr data and lists them in corresponding boxes for “Initial melt” in the first dropdown box (Figure 1c). The user may also choose alternative normalized standards provided in the dropdown box, for example, C1, E-MORB, N-MORB, and OIB standards of Sun and McDonough (1989) and upper, lower, and bulk continental crust and oceanic crust standards of Taylor and McLennan (1985), to calculate  $(Ce/Ce^*)_D$  values.  $Ce^{4+}/Ce^{3+}$



**Figure 3.** Flowcharts summarizing the basic workflow for calculating thermodynamic parameters on the basis of the composition of zircon and its host melt (or rock). Meanings of different colored boxes are as in Figure 2. NNO = Ni-NiO buffer; FMQ = fayalite-magnetite-quartz buffer; HM = hematite-magnetite buffer.

ratios are synchronously calculated with  $(\text{Ce}/\text{Ce}^*)_{\text{D}}$  values through similar processes. The second dropdown box in the “Choose Standards” subpanel provides two similar sets of radii data (Shannon, 1976), namely, the “R(A)-1” (crystal radius) and “R(A)-2” (effective ionic radius), for use in calculating  $(r_i/3 + r_o/6) \times (r_i - r_o)^2$  for the  $(\text{Ce}/\text{Ce}^*)_{\text{D}}$  calculation (equation (8)). The user may also enter other numbers in the input boxes, from which the program will calculate new  $(\text{Ce}/\text{Ce}^*)_{\text{D}}$  values. Finally,  $f\text{O}_2$  is calculated on the basis of temperature and  $(\text{Ce}/\text{Ce}^*)_{\text{D}}$  (Figure 3).

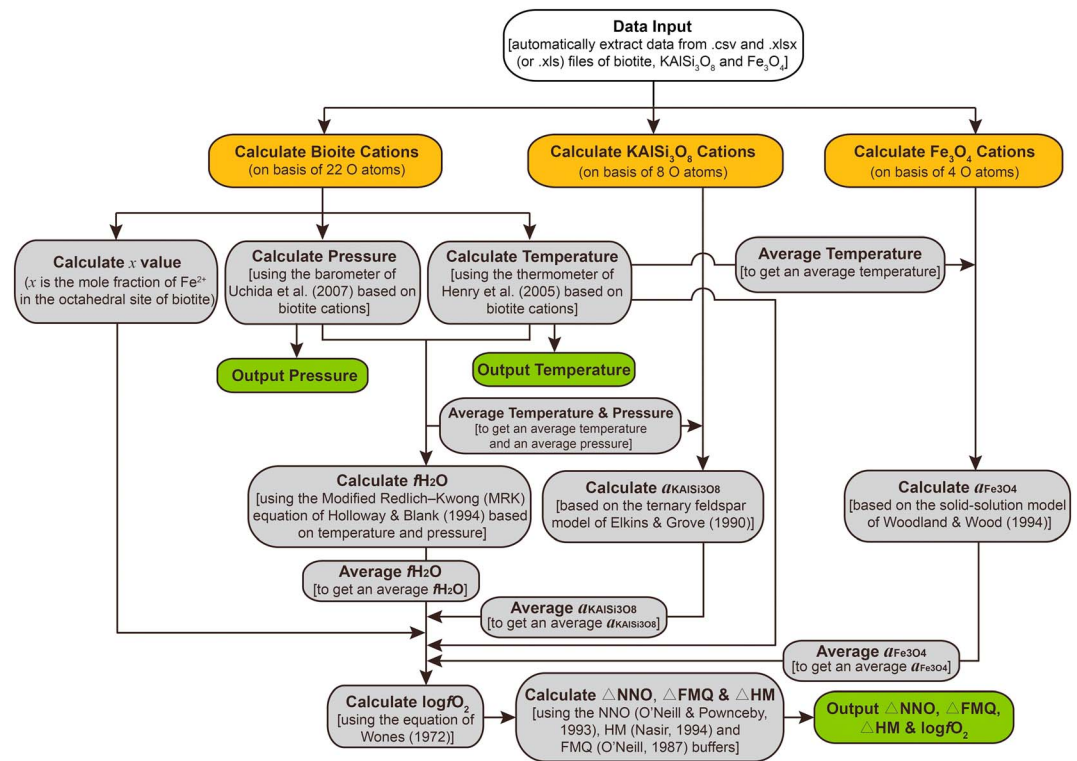
### 3.2.3. Biotite

Calculations for biotite are based on EMPA data for biotite, K-feldspar, and magnetite. Again, the first step converts oxides to cations on the basis of mineral formulae. Cation data are then used in calculations as shown in Figure 4.

Then three parallel calculations are performed using cation composition of biotite, for  $x$  value,  $P$ , and  $T$  (Figure 4). The user can run multiple biotite, magnetite, and K-feldspar at the same time, and they will not be cross-correlated. However, the three minerals must all be from the same rock. Calculated  $T$  and  $P$  results by biotite compositions will be averaged and combined in the subsequent calculation of  $a_{\text{KAlSi}_3\text{O}_8}$  values with cation components of K-feldspar (Figure 4). Meanwhile,  $a_{\text{Fe}_3\text{O}_4}$  values are calculated using average  $T$  and cation components of magnetite, and  $f\text{H}_2\text{O}$  is calculated using equation (13) with calculated individual temperature and pressure based on each biotite composition (Figure 4). Finally,  $f\text{H}_2\text{O}$ ,  $a_{\text{KAlSi}_3\text{O}_8}$ , and  $a_{\text{Fe}_3\text{O}_4}$  will be averaged and used to calculate  $f\text{O}_2$  with  $x$  value and  $T$  by using equation (12) (Figure 4).

### 3.3. Data Output

To save calculated results, the user clicks the “Save Result” button for each mineral subinterface (Figures 1b–1d) and selects the desired folder. The program creates Excel tables (.xlsx files) as default saved files.

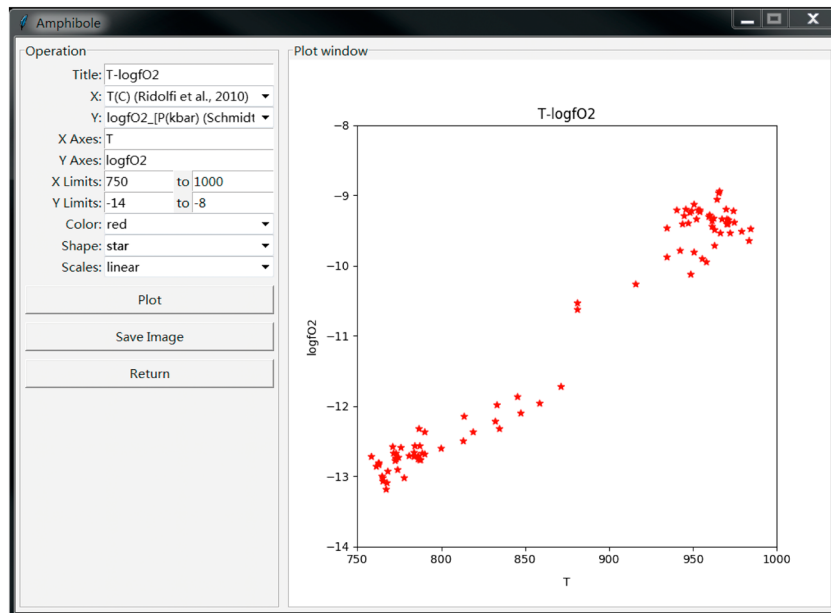


**Figure 4.** Flowcharts summarizing the basic workflow for calculating mineral cations and thermodynamic parameters on the basis of biotite, K-feldspar, and magnetite. Note that the used temperature values in the last step of  $\log fO_2$  calculation are the calculated individual temperature based on each biotite composition. Meanings of different colored boxes are as in Figure 2. NNO = Ni–NiO buffer; FMQ = fayalite-magnetite-quartz buffer; HM = hematite-magnetite buffer.

### 3.4. Plotting

The user may enter the plotting interface via the “Plot” button (Figure 1). Plotting and graphic capabilities of the program are based on Matplotlib modules (Hunter, 2007). As an example, the plotting interface for amphibole is divided into a left “Operation” panel and right plot window (Figure 5). The user selects X and Y coordinate axes from the dropdown menu in left “Operation” panel, with these axes sharing the same options, including calculated mineral compositions and thermodynamic parameters ( $T$ ,  $P$ , and  $fO_2$ ). The user can respectively rename X and Y axes through manual input boxes (i.e., “X Axes” and “Y Axes”) under dropdown menu boxes of X and Y (Figure 5), though the initial name of X and Y axes in the rename box is set to the same as that selected in the dropdown menu. Axes ranges are set in the “X Limits” and “Y Limits” boxes (Figure 5). A figure title can be entered in the “Title” box, with linear or logarithmic scales set in the “Scales” box (Figure 5). Symbols of different color and shape can be selected via the “Color” and “Shape” dropdown menu boxes (Figure 5). After the user chooses linear or logarithmic scale, the program will automatically judge which axes can be converted to linear or logarithmic scale. Note that the logarithmic scale does not apply to all chosen axes. For instance, the calculated  $\log fO_2$  value is often less than 0, the logarithmic scale for such a negative  $\log fO_2$  axis does not work and no data will be shown in the right plot window.

Once axes and symbols are set, the user clicks the “Plot” button to plot data on the binary diagram in the right plot window (Figure 5). Axes and symbols can be adjusted in the left panel before saving the image. However, contents of boxes in left “Operation” panel may be modified many times by the user, clicking the “Plot” button displays each modified contents in plot window. The “Save Image” button allows saving of the image in the Scalable Vector Graphics (SVG) format. The SVG image may be edited in Adobe Illustrator, Adobe Photoshop, CorelDRAW, or other image-processing software. The commonly used model diagrams are provided in the supporting information diagram file so that the user can use these when modifying saved SVG images.



**Figure 5.** Plotting subinterface of amphibole showing the procedure to plot the binary diagrams. Data source is Table S8.

## 4. Calculation Examples

### 4.1. Amphibole

Take the 91 given amphibole data from Jiru, Qulong, and Jiama deposits in Tibet (Table S8; Wang et al., 2014) as an example, the user can copy them from Table S8 and paste them into the model input Excel Table S2 of amphibole and save data. Through the subinterface of amphibole (Figure 1b), the user loads filled Table S2 and calculates various parameters by clicking the “Calculate” button.

Amphibole of Tibetan samples comprises Tschermakite, Mg-hastingsite and Mg-amphibole. The calculated temperatures and H<sub>2</sub>O contents for amphiboles are 758–984 °C and 2.9–6.5 wt.%, respectively (Table S8). Pressure values calculated by equation (3) range from 0.7 to 5.3 kbar (corresponding to a continental depth of 2–20 km), while values calculated by equation (5) range from 1.1 to 8.0 kbar (corresponding to a continental depth of 4–30 km). Based on the two pressure values, Geo-*f*O<sub>2</sub> will provide two sets of *f*O<sub>2</sub> value ( $\Delta$ FMQ), respectively, +0.8 to +2.7, and +1.0 to +2.8 (Table S8).

### 4.2. Zircon

Trace element data and calculated results of zircon from Jiru (JR) and Xueba (XB) area in Tibet (Wang et al., 2014) are provided in Table S9. Table S9 also contains three corresponding bulk component data of JR-2, JR11-06, and XB-12. As mentioned above, Geo-*f*O<sub>2</sub> has no automatic matching function, so the user needs to calculate *f*O<sub>2</sub> values of JR-2, JR11-06, and XB-12 separately. For example, the user can copy bulk component data of JR-2 and three trace element data of zircons (i.e., JR-2\_3, JR-2\_4, and JR-2\_5) yielded in rock JR-2 from Table S9 then respectively paste them into the model input Excel Tables S4 and S3 and save data. By inputting Tables S4 and S3 through the zircon subinterface, the user can obtain Ce<sup>4+</sup>/Ce<sup>3+</sup> ratio (82–119; Table S9), temperature, and *f*O<sub>2</sub> values of JR-2. As Geo-*f*O<sub>2</sub> contains three thermometers of zircon (Ferry & Watson, 2007; Miller et al., 2003; Watson & Harrison, 1983), three sets of *f*O<sub>2</sub> values (i.e.,  $\Delta$ FMQ = +3.73 to +5.13; +3.69 to +5.09; +3.07 to +4.67; Table S9) therefore will be calculated respectively based on three temperature results (i.e., 734–735 °C; 733 °C; 708–740 °C; Table S9). Then calculated temperature and *f*O<sub>2</sub> values will be saved in output file by clicking the “Save Result” button in zircon subinterface (Figure 1c). Through repeating above calculation procedure, the user can respectively get Ce<sup>4+</sup>/Ce<sup>3+</sup> ratio, temperature, and *f*O<sub>2</sub> values of sample JR11-06 and XB12-3 (see results in Table S9). In order to avoid error caused by incorrect operation, only column B in Table S4 is allowed to input the only one set of bulk component data at one time, while other columns are locked.

### 4.3. Biotite

Table S10 contains EMPA data and calculated results of biotite, K-feldspar, and magnetite from the Pulang deposit (Li et al., 2019). Each example of each mineral are from the same rock sample (i.e., 15PL-04; Li et al., 2019).

As calculation in biotite section does not require cross correlation among data of three minerals, the user can paste the six given EMPA data (Table S10) of biotite into model input Excel Table S5, the five given EMPA data of K-feldspar into Table S6, and the three given EMPA data of magnetite into Table S7 and save data in each table. After input Tables S5, S6, and S7 in biotite subinterface (Figure 1d), the user can get the crystallization temperature and pressure of biotite ( $T = 731\text{--}748\text{ }^{\circ}\text{C}$ ;  $P = 0.9\text{--}1.1\text{ kbar}$ ; Table S10). The average temperature and pressure ( $741\text{ }^{\circ}\text{C}$  and  $1.0\text{ kbar}$ ) will be joined into the calculation of  $f\text{H}_2\text{O}$ ,  $\alpha_{\text{KAlSi}_3\text{O}_8}$ , and  $\alpha_{\text{Fe}_3\text{O}_4}$ . Finally, the  $f\text{O}_2$  values ( $\Delta\text{FMQ} = +1.1\text{ to }+1.5$ ; Table S10) will be calculated through equation (12).

## 5. Summary

Geo- $f\text{O}_2$  is specialized software for calculating and visualizing magmatic  $f\text{O}_2$  based on oxybarometers and thermobarometers for amphibole, zircon, and biotite in intermediate-silicic magmas. It runs in Windows platforms and requires no installation. It automatically extracts data from Excel tables or .csv files, with calculated results being displayed in Excel tables. With user-friendly interfaces, it is able to plot data on many different binary diagrams, which may be saved in SVG format.

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