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AMFORM, a new mass-based model for the calculation of the unit formula of amphiboles from Electron Micro-Probe analyses: calibration, recommendations and implications
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AMFORM, a new mass-based model for the calculation of the unit formula of amphiboles from Electron Micro-Probe analyses: calibration, recommendations and implications

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Abstract

In this work, we have studied the relationships between mass concentration and unit formula of amphibole using 114 carefully selected high-quality experimental data (EMP+SREF±SIMS analyses) of natural and synthetic Li-free monoclinic species belonging to the Ca and Na-Ca subgroups, plus Li-free and Mn-free $C2/m$ end-members (a total of 75 ideal element oxides-formula pairs including some oxo analogues of Ca amphiboles). Theoretical considerations and regression analysis of these data allowed us to obtain a number of equations which can be used to: (i) calculate from EMP analyses a amphibole unit-formula consistent with SREF±SIMS data, (ii) discard unreliable analyses and (iii) estimate $^W O^{2-}$ and Fe^{3+} contents in Li-free $C2/m$ amphiboles with relatively low Cl contents (≤0.2 atoms per formula unit). The AMFORM approach mostly relies on the fact that while the cation mass

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in Cl-poor amphiboles increases with the content of heavy elements, its anion mass maintains a nearly

constant value, 22O + 2(OH, F, O), resulting in a very well-defined polynomial correlation between the

molecular mass and the cation mass per gram (R^2 = 0.998). The precision in estimating the amphibole

formula is 2-4 times higher than that of classic methods which follow IMA-recommended schemes. A

linear relation between the $^WO^{2-}$ content and the sum of some ^{C}(Ti, Fe^{3+}) and ^{A}(Na+K) contents, useful

to estimate the iron oxidation state of highly-oxidized amphiboles typical of post-magmatic processes,

is also proposed. A user-friendly spreadsheet (AMFORM.xlsx) is provided as supplementary material.

This work opens new perspectives on the unit-formula calculation of other minerals containing OH and

structural vacancies (e.g. micas).

Keywords

Li-free amphiboles · unit-formula calculation · oxo component · cation mass · SREF · SIMS

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Introduction

Amphiboles are a supergroup of silicate minerals containing, either at the major- or at the trace-element

level, most elements of geological/geochemical relevance (for a review, see Hawthorne et al. 2007). It

has been largely recognized that the role of amphibole in understanding geological/planetary processes

and several health issues is of crucial importance (e.g. Forbes and Starmer 1974; Foley et al. 2002;

Gunter et al. 2007; McCanta et al. 2008; Jackson et al. 2013; Smith 2014). Amphibole crystal-

chemistry has captured the attention of many scientists over the years because of its intrinsic

complexity (consider that even the term amphibole derives from the Greek "αμφιβολος", which means

ambiguous; Réné J. Haüy 1743 – 1822; Cipriani et al. 2007), its remarkable compliance to incorporate

most elements of geological interest and ability to record the steps of a wide range of geochemical and petrological processes due to a network of mutual relationships between cation ordering, chemistry of the associated phases (minerals and/or melt) and intrinsic parameters such as pressure, temperature and fugacity of volatile elements (Holland and Blundy 1994; Al´meev et al. 2002; Oberti et al. 2000, 2007a; Ridolfi et al. 2010; Ridolfi and Renzulli 2012; Zhang et al. 2017). However, the prerequisite for using amphiboles as geological markers is the determination of their correct crystal-chemical formula (i.e., composition and site partitioning). Routine calculations of amphibole unit-formulae from Electron Micro-Probe (hereafter EMP) data may be seriously affected by inappropriate normalization procedures and/or the lack of accurate information on the oxidation state of iron and the contents of hydrogen and lithium (Leake et al. 1997; Al´meev et al. 2002; Hawthorne et al. 2012; Locock 2014).

In this work, we analyze the relation between elemental concentration (by mass) and stoichiometry in the amphibole supergroup, and propose a new mass-based method, to be applied to the only EMP data, that allows identification of bad analyses and calculation of the correct unit formula of Li-free (and Mn- and Cl-poor) $C2/m$ amphiboles, with an uncertainty 2-4 times lower than that of other published procedures (Hawthorne et al. 2012; Locock 2014).

Definitions

The amphiboles are a supergroup of silicate minerals with the general formula $AB_2C_5T_8O_{22}W_2$ (Hawthorne et al. 2012). The group cations considered in this work include: A = Na, K, Ca, □ (vacancy); B = Ca, Na, Mn^{2+}, Fe^{2+}, Mg; C = Mg, Ti^{4+}, Fe^{2+}, Mn^{2+}, Cr, Ni, Zn, Al, Fe^{3+}; T = Si, Al, Ti^{4+}; and W = OH^-, F, Cl, O^{2-} (where Mn, Cr, Ni, Zn and Cl are minor components, ≤ 0.2 atoms per formula unit, apfu).

Below we report operative definitions useful to follow the text more easily. The sign $\sum$ includes all the cations and/or anions in the groups defined above; e.g. $\sum_{A}^{T} x=$ sum of the parameter x for all A-, B-, C- and T-group cations, $\sum_{A}^{W} x=$ sum of the parameter x for A-, B-, C- and T-cations plus W-anions and 22 O^{2-} pfu.

- *total element oxides*: sum of cation oxides and halogens calculated excluding the measured FeO_{tot} (total iron content) and the oxygen atoms balancing F and Cl (i.e. $O^{F,Cl}$), and adding Fe_2O_3, FeO and H_2O calculated from the unit-formula, corresponding to the H_2O measured by Secondary-Ion Mass Spectrometry (hereafter SIMS) or estimated by Single-crystal X-ray Structure REFinement (hereafter SREF). Note that the total element oxides of EMP analyses generally deviates from ideality (100 wt%);

- *original composition*: the concentrations expressed as wt% of the oxides (SiO_2, TiO_2, Al_2O_3, Cr_2O_3, FeO_{tot}, NiO, ZnO, MnO, MgO, CaO, Na_2O, K_2O) and halogens (F, Cl) in the amphibole formula, usually measured by EMP analyses;

- *normalized composition*: the concentrations expressed as wt% of the cation oxides (SiO_2, TiO_2, etc.) and halogens (F, Cl) in amphibole calculated from the unit formula to obtain a value of the total element oxides equal to 100 wt% (e.g. Table 1 and http://webmineral.com for end-members);

- *deviated composition*: the concentrations (wt%) of the cation oxides (SiO_2, TiO_2, etc.) and halogens (F, Cl) in amphibole forced to have a value of the total element oxides deviating from 100 wt%, specifically 98.2 and 101.8 wt%;

- *TC*: total coefficient, obtained by dividing the sum of the cation oxides (with iron as FeO_{tot}) of a normalized composition with that of its original or deviated compositions; TC is used to modify the original composition to obtain an adjusted composition approaching a normalized composition (see following sections);

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- M_r: molecular mass of amphibole usually calculated from its unit formula, i.e. $Mr = \sum_A^W apfu \times A_r$, where A_r is the atomic mass of all elements in the formula;

- *cmpg*: cation mass per gram, calculated from the original, deviated or normalized compositions, i.e. $cmpg = 10^{-2} \sum_A^T wt\%$. Note that *cmpg* is actually a mass ratio and thus for normalized compositions it corresponds to the total cation mass divided by the sum of the total cation and anion masses;

- X_i: cation mass fraction of element i, that is the mass of element i divided by the total cation mass (e.g $X_{Si} = \frac{Si\,wt\%}{\sum_A^T wt\%}$, $X_F = \frac{F\,wt\%}{\sum_A^T wt\%}$); they are the same in normalized, deviated and original compositions;

- *CR*: correlation ratio between the apfu and *mmol/g* (millimole per gram) of the total cations, i.e. $CR = \frac{\sum_A^T apfu}{\sum_A^T mmol/g}$. *CR* is a constant value for any normalized composition and, once precisely determined (see below), can be easily used to calculate the apfu of each element multiplying *CR* by the element concentration (*mmol/g*);

- *Δcharge*: deviation from electroneutrality in an amphibole unit-formula (i.e. positive − negative charge sums);

- *ΔC* and *ΔB*: deviation from 5 apfu and 2 apfu in the C- and B-group cations, respectively.

Data selection and techniques

Composition and petrogenesis of the investigated amphiboles

We have studied the relationships between concentration and unit formula in Li-free and Mn,Cl-poor monoclinic amphiboles belonging to the Ca, Na-Ca subgroups (and some of their oxo analogues) based on a dataset accurately selected in the literature and in the CNR-IGG amphibole database, according to

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the presence of accurate EMP+SREF±SIMS analyses. The dataset contains 114 oxides-formula pairs with the largest possible geochemical and geological variability; the oxo-amphiboles considered are kaersutite, ferri-kaersutite, oxo-potassic-chromio-katophorite, oxo-potassic-taramite, Ti-rich oxo-sadanagaite, Ti-rich oxo-pargasite and Ti-rich oxo-ferri-pargasite (see AMFORM.xlsx). Na amphibole species were excluded because they may contain minor to moderate amounts of Li (e.g. Hawthorne et al. 1993) which cannot be detected and measured by EMP analysis.

The dataset includes published oxides-formula pairs of 61 synthetic (Oberti et al. 2000; Bottazzi et al. 1999; Tiepolo et al. 2000; 2003; Adam et al. 2007) and natural amphiboles which are typical of geologically relevant systems (gabbro, peridotite, lherzolite, kyanite-eclogite, marble, metasomatic/skarn-type deposit and several types of metavolcanic amphibolites) and coming from different world-wide localities (Oberti et al. 1995; Vannucci et al. 1995; Robinson et al. 1997; Oberti et al. 2007b; Uvarova et al. 2007; Perinelli et al. 2012; Della Ventura et al. 2014). The unpublished oxides-formula pairs (53) come from the CNR-IGG database in Pavia and include amphiboles from volcanic deposits, mantle ultramafic rocks (hornblendites, pyroxenites, peridotites), peridotitic and pegmatitic veins.

Characterizing methods

All the unpublished amphiboles were analyzed by EMP, SREF and SIMS allowing a complete characterization of their crystal-chemical parameters. SREF and SIMS analyses were done at IGG-CNR in Pavia, while EMP analyses were mostly done at the University of Manitoba (Winnipeg, Canada).

The crystal-chemical formulae were calculated by combining SREF, EMP and SIMS results. The number of A cations was estimated on the basis of the refined site-scattering values at the relevant sites and from K_2O and Na_2O contents from EMP analysis. The oxo component was evaluated either by SIMS or by a SIMS-calibrated crystal-chemical relationship (Oberti et al. 2007a), so that the Fe^{3+}

content can be derived based on the overall electroneutrality. The Fe^{3+} content and its distribution were further constrained through the pattern of refined mean bond-lengths observed at the three $M(1-3)$ octahedra. The presence of the $M(4')$ subsite, indicating the occurrence of small B cations (Mn^{2+}, Fe^{2+}, Mg), was checked on the difference Fourier maps. B cations were calculated assigning excess C cations (first Mn^{2+} and then Fe^{2+} and Mg) to minimize the difference between the site scattering calculated (from EMP) for the B and C cations and those obtained by SREF. As a further check, the ^{T}Al contents obtained by recalculation of EMP analyses are in close agreement with those calculated from the refined $<T(1)-O>$ and $<T(2)-O>$ distances (Oberti et al. 2007a).

Many of the amphiboles taken from the literature include EMP, SREF and SIMS data, and their formulae were obtained following the same procedure. The amphibole formula selected from the article of Robinson et al. (1997) was derived from EMP, SREF, Mössbauer (for Fe^{3+}/Fe_{tot}), wet-chemical (for F) and IR (InfraRed spectroscopy, for H_2O) analyses. In some cases, the formulae were derived from EMP and SREF data only (Oberti et al. 1995; Vannucci et al. 1995; Oberti et al. 2007b; Della Ventura et al. 2014), and the oxo component was estimated using a correlation developed at CNR-IGG in Pavia based on SREF results (Oberti et al. 2007a). In other cases, the Fe^{3+} content of the amphibole was validated by Mössbauer spectroscopy (Uvarova et al. 2007, Perinelli et al. 2012). The amphibole data selected from the older article (Oberti et al. 1995) the occurrence of $^{W}O^{2-}$ in amphibole was estimated during this work using the published SREF data (see above).

Selection criteria of the calibration data

Both literature and unpublished amphiboles were processes using a series of criteria to guarantee as much as possible the selection of a calibration dataset characterized by high-quality data.

We first discarded amphibole compositions showing standard deviations (σ) of the EMP element oxides higher than 2/3 of the average oxide σ values for the experimental amphiboles reported in Table 2 of Ridolfi and Renzulli (2012). We discarded also the amphibole compositions with total

element oxides falling outside the range of 100±1.7 wt%, because large deviations from 100 wt% may derive from analytical problems for some elements, resulting in error propagation to the unit formula. The amphibole compositions in the dataset have total element oxides ranging from 98.3 to 100.8 wt% although most of the totals are lower than 100 wt%, with an average value of 99.3 wt%.

Amphibole formulae showing *Δcharge* larger than ±0.05, ΔC and ΔB larger than ±0.01 and/or total cations higher than 16.005 apfu were also discarded. In addition, formulae calculated without considering the oxo component, i.e. forcing the negative charges to be 46, were not considered. The bijection between the composition and formula of any amphibole was carefully checked comparing the *CR* values for each major cations (e.g. $CR^{Si} = \frac{Si\ apfu}{Si\ mmol/g}$) with the *CR* calculated on the total cation sum (as defined above). This procedure allowed us to avoid mismatches between formulae and compositions due to adjustment and/or editing.

This final database contains 114 entries and is included in the AMFORM.xlsx spreadsheet (provided as supplementary material). The ranges in elemental composition are: Si = 5.8-7.8 apfu; ^{A}(Ca+Na+K) = 0.1-1.0 apfu; F ≤ 1.3 apfu; Cl ≤ 0.2 apfu; Mg/(Mg+Fe^{2+}) = 0.2-1.0; Fe^{3+}/Fe$_{tot}$ = 0.0-1.0.

It is worth noting that oxides-formula pairs not validated by SREF were not included in the final dataset. This decision was taken to guarantee an independent check of the formulae and a reliable constraint on the total number of cations.

Beside the 114 selected amphibole compositions, we used ideal formulae and compositions of selected Li- and Mn-free *C*2/*m* end-members of the amphibole supergroup (Hawthorne et al. 2012) (Table 1). The 75 oxides-formula pairs in Table 1 also include kaersutite, ferri-kaersutite, ferro-kaersutite, ferro-ferri-kaersutite and some oxo analogues of the Ca groups as these amphiboles in nature may often have a significant oxo-component.

Rationale and data analyses

The high-quality dataset described above was used to analyze any possible relation between compositional (e.g. wt% and *mmol/g*) and unit-fomula parameters in amphiboles.

For a complete characterization of the amphibole unit-formula, two crucial parameters must be determined: the total cation content (ranging from 15 to 16 apfu) and the oxo component ($^WO^{2-}$), which allows the sum of the negative charges to vary between 46 and 48. When these parameters are known and the presence of Mn^{3+} can be excluded, the amount of Fe^{3+} can be obtained under the constraint of electroneutrality.

Development of the *CR*-equations

The correlation ratio (*CR*) between apfu and *mmol/g* of any component or sum of components (e.g. Si, total aluminium Al_T, F, total cations) must be constant for any normalized and end-member composition-formula pair. If *CR* is known with a reasonably good approximation, the apfu content of each element can be calculated multiplying *CR* by its concentration in *mmol/g*.

Figure 1a shows that the *CR* of the normalized and end-member compositions is perfectly correlated with their molecular mass, M_r:

$$CR = 10^{-3}M_r \qquad\qquad (R^2 = 1.000) \qquad\qquad (1)$$

The original compositions only slightly deviate from this linear trend. The deviations is due to the total element oxides which are usually are lower than 100% (see above). In Figure 1a, the end-member sample with the lowest M_r is cummingtonite, $\square Mg_2Mg_5Si_8O_{22}(OH)_2$, and that with the highest M_r is ferro-ferri-cannilloite, $CaCa_2(Fe^{2+}_4Fe^{3+})(Si_5Al_3)O_{22}(OH)_2$.

Note that equation 1 is valid for any type of mineral or compound, and should be used at the end of any formula calculation procedure to validate the final results and the quality of the data (see

below). However, this simple correlation cannot be used to estimate CR from EMP analysis because M_r can only be calculated from the formula.

Figure 1b shows that the CR values of normalized and end-member compositions have a nearly perfect polynomial relation with the cation mass per gram, $cmpg$, which can be directly calculated from EMP data (see above):

$$CR = 4.809\,cmpg^2 - 3.409\,cmpg + 1.276 \qquad\qquad (R^2 = 0.998) \qquad\qquad (2)$$

Indeed, the anion components in the different amphibole compositions have almost the same mass, because they mostly consist of the same number of ions with similar A_r, $22O^{2-} + 2(OH^-, F^-, O^{2-})$. In contrast, the mass of the cation component increases with the amount of heavier cations (e.g. Fe^{2+}, Fe^{3+}) resulting in a progressively increasing pattern of CR (and M_r) with $cmpg$. Because $cmpg$ is a mass ratio, Figure 1b has a curvilinear trend, in agreement with the general rules for correlations in mixing binary systems (Langmuir et al. 1978). The small scattering observed for some normalized and end-member compositions ($R^2 = 0.998$; Fig. 1b) is due to the occurrence of $^W(Cl^-, F^-, O^{2-})$, which have A_r different from that of OH^-, thus affecting the $cmpg$ values. For example, the heaviest end-member ferro-ferri-cannilloite has the same cation mass of its oxo analogue but a higher M_r value because it differs (in mass term) by having two more hydrogen atoms (Table 1). Therefore, the mass of W anions is higher than that of its oxo equivalent (because OH^- is heavier than O^{2-}) resulting in a $cmpg$ value slightly lower than that of oxo ferro-ferri-cannilloite (Fig. 1b; Table 1). F-rich amphiboles behave in the opposite way because F^- has a mass higher than OH^-. However the effect of $^WF^-$ and $^WO^{2-}$ in calculating CR is minimal as confirmed by the high determination coefficient (R^2) of equation 2 (Fig. 1b), so that amphibole compositions with high F and oxo contents can be treated with this method with a sufficient accuracy.

In contrast, amphiboles with high Cl contents (e.g. Ridolfi et al. 2010) deviate significantly from equation 2 (towards lower $cmpg$) because the A_r of chlorine is about twice that of F, OH and O.

However, the maximum Cl content in the high-quality analyses of amphiboles is 0.20 apfu (corresponding to 0.72 wt%) and does not produce large deviations from equation 2. This is because the incorporation of Cl in amphibole is related to high Fe^{2+} contents (e.g. Oberti et al. 2007a) which results in relatively low *cmpg* underestimations (e.g. in the two Fe- and Cl-rich amphiboles marked with green triangles in Fig. 1b).

It is worth noting that equation 2 cannot be successfully applied to the original compositions of most of the amphiboles because EMP uncertainties commonly result in incorrect *CR* and *cmpg* values leading to significant deviations from the normalized composition, i.e. from total element oxides equal to 100 wt% (Fig. 1). Therefore, at least a preliminary estimation of $^{W}O^{2-}$ and H_2O is required. This issue is discussed in more detail in the section "Total coefficient and calculation procedure".

The oxo component, $^{W}O^{2-}$

It is commonly accepted that $^{W}O^{2-}$ and $^{W}OH^{-}$ contents in amphibole mostly depend on two substitution mechanisms involving cations occurring at the $M(1)$ and $M(3)$ sites:

$$^{M(1)}(Mg, Fe^{2+}) + 2^{W}OH^{-} \rightarrow {}^{M(1)}Ti^{4+} + 2^{W}O^{2-} \qquad \text{(a)}$$

$$^{M(1,3)}Fe^{2+} + {}^{W}OH^{-} \rightarrow {}^{M(1,3)}Fe^{3+} + {}^{W}O^{2-} \qquad \text{(b)}$$

During igneous and metamorphic processes, the OH^{-} content of amphibole is mostly ruled by substitution mechanism (a) wherein the amount of OH^{-} at the W site is reduced by twice the amount of Ti incorporated at the $M(1)$ site. Substitution (a) mostly occurs at high-T low-fH$_2$O conditions, and involves chemical exchange of major components such as Mg, Fe^{2+} and Ti with the surrounding environment (glass, minerals). During magma ascent or hydrothermal alteration, amphibole may undergo a high T-fO_2 process of deprotonation involving iron oxidation according to substitution mechanism (b) (e.g. King et al. 1999; Oberti et al. 2007a, Popp et al. 2006).

From a crystal-chemical viewpoint, the occurrence of $^{W}O^{2-}$ implies important changes in the cation-ordering scheme typical of amphiboles, where high-charged C cations fully ordered at the $M(2)$

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site, with the only exception of Al, which may disorder between the M(2) and M(3) sites in high-T Mg-rich pargasites and edenites (Oberti et al 1995; Della Ventura et al 2014). The different bond-valence bond-strength requirements of the O(3) oxygen after H^+ loss must be satisfied by the presence of high-charged cations at the coordinated M(1) (with multiplicity 2) and M(3) sites. This feature implies complex but strongly related compositional changes in the amphibole solid-solution system, that can be empirically approached using multivariate least-square analysis (Ridolfi and Renzulli 2012; Ridolfi et al. 2014; Zhang et al. 2017).

Among the 114 amphiboles in the dataset, 87 formulae have $^WO^{2-} \leq 2\ ^CTi$ implying that mechanism (b) is almost not active. Hereafter, for these amphiboles we will use the prefix "poorly-oxidized" to remind that the amount of $^{M(1,3)}Fe^{3+}$ due to post-crystallization oxidation is zero or very low. These amphiboles may contain up to 1.3 apfu $^WO^{2-}$, which mostly derives from the substitution mechanism (a). However, the use of total Ti in C (^CTi) as a proxy for the oxo component (Hawthorne et al. 2012; Locock 2014) may be severely misleading because in these samples a significant amount of ^CTi is often ordered at the M(2) site and hence does not contribute to reaction (a) (Oberti et al. 2007a).

Regression analysis shows that the $^WO^{2-}$ content in poorly-oxidized amphiboles (with $^WO^{2-} \leq 2^CTi$) can be estimated with reasonably low errors (Fig. 2a) using the following equation:

$$^WO^{2-} = -6.684X_{Si} + 11.025X_{Ti} - 0.989X_{Al} - 2.800X_{Fe} - 20.359X_{Mn} - 0.903X_{Mg} - 6.875X_{Ca} -$$
$$11.119X_{Na} - 2.553X_K + 5.751X_F + 4.610\ (apfu) \tag{3}$$

This equation can be applied without any previous calculation of the amphibole formula, as it only depends on the values of cation fraction (X_i) calculated from EMP analyses. In addition, the X_i values are the same in both original and normalized compositions because generalized overestimation/underestimation does not change the mass ratios (see above). The statistic error σ_{est} (standard error of estimate) for poorly-oxidized amphiboles (0.10 apfu; Fig. 2a) is comparable to SIMS

uncertainty in hydrogen measurement (±10% relative; e.g. Oberti et al. 2007a) supporting the validity of equation 3.

A drawback of equation 3 is that it underestimates $^{W}O^{2-}$ in highly-oxidized amphiboles (where $^{W}O^{2-} > 2^{C}Ti$), which underwent high-T, high-fO_2 post-magmatic and/or hydrothermal alteration according to mechanism (b). However, this issue may even turn out to be an advantage when studying the processes of amphibole magmatic crystallization (e.g. Ridolfi et al. 2010; Ridolfi and Renzulli 2012; Ridolfi et al. 2016; Zhang et al. 2017). In fact, the higher value of fO_2 in high-T magmatic environments (~10^{-7} bar, corresponding to a logfO_2 of 3-4 units above the Ni-NiO buffer; Ridolfi and Renzulli 2012) is several orders of magnitude lower than in air (~0.21 bar, i.e. -0.68 logfO_2; Namur et al. 2012) where high-T post-magmatic oxidation most probably occurs. It is worth noting that the highly-oxidized amphiboles in our database are Ca-dominant megacrysts (rapidly ejected to the surface from high T-P conditions) or mantle amphiboles which underwent hydrothermal alteration.

At this point, we looked for correlations between the measured values of $^{W}O^{2-}$ and cation compositional parameters in both poorly and highly oxidized amphiboles, starting from the observation that the fractions of Ti and Fe^{3+} occurring at the $M(1)$ and $M(3)$ sites are directly involved in the process of deprotonation. The best correlation we found is reported in Figure 2b for the 114 amphiboles in the dataset, i.e. $^{W}O^{2-} = 0.963[4/3^{C}Ti + 2/3^{C}Fe^{3+} + 2/3^{A}(Na+K)] − 0.624$. The overall correlation shows a reasonably good R^2 value (0.927) and closely approaches the equation:

$$^{W}O^{2-} = 4/3^{C}Ti + 2/3^{C}Fe^{3+} + 2/3^{A}(Na+K) – 2/3 \text{ apfu} \tag{4a}$$

Equation 4a works well for both poorly ($^{W}O^{2-} \leq 2^{C}Ti$) and highly ($^{W}O^{2-} > 2^{C}Ti$) oxidized amphiboles when $4/3^{C}Ti + 2/3^{C}Fe^{3+} + 2/3^{A}(Na+K)$ is $\geq 2/3$. In that region, the only two samples significantly deviating from equation 4a ($^{W}O^{2-}$ overestimation up to 0.49 apfu) are rare and peculiar Na-Ca amphiboles, i.e. alumino-taramite K22-2 and fluoro-alumino-magnesio-taramite DJ102-23, which are

characterized by high $^C Fe^{3+}$ and A-cations contents but, according to their crystal-chemical characterization do not contain oxo component (Oberti et al. 2007b; Fig. 2b).

In Figure 2b, amphibole compositions with $4/3 \, ^C Ti + 2/3 \, ^C Fe^{3+} + 2/3 \, ^A(Na+K) \leq 2/3$ have zero or negligible $^W O^{2-}$ contents, providing the constraint:

$$^W O^{2-} = 0 \text{ apfu when } 4/3 \, ^C Ti + 2/3 \, ^C Fe^{3+} + 2/3 \, ^A(Na+K) \leq 2/3 \text{ apfu} \tag{4b}$$

When applying equations 4a and constraint 4b we obtain a $\sigma_{est} = 0.12$ apfu in the whole dataset (Fig. 2b). This error is also consistent with the error in H measurements by SIMS ($\pm 10\%$ relative), thus supporting the validity of our approach. When the two major outliers alumino-taramite K22-2 and fluoro-alumino-magnesio-taramite DJ102-23 are not considered, the maximum error decreases from 0.49 to 0.3 apfu which is even lower than that indicated by equation 3 for the only poorly-oxidized amphiboles (0.4 apfu; Fig. 2a).

Equation (4a) and constraint (4b) can be easily applied to any amphibole unit-formula anytime an independent measurement of Fe^{3+}/Fe_{tot} is available. When this is not the case, $^W O^{2-}$ and Fe^{3+} contents can be estimated using a system of two linear equations including (4a) and the charge balance equation:

$$4(Si+Ti) + 3(Al+Cr+Fe^{3+}) + 2[Mg+(Fe_{tot}-Fe^{3+})+Mn+Ni+Zn+Ca] + Na+K = 46 + {}^W O^{2-} \tag{4c}$$

where the uncertainty of the $^W O^{2-}$ and Fe^{3+} estimates depends on the errors of cation estimation multiplied by their ionic charge.

The presence of the A cations in equations 4a,b may be explained by their capability to help in the local electroneutrality around the O(3) site, where deprotonation occur. Recent *in operando* studies combining SREF and FTIR (Fourier Transform Infrared Spectroscopy) showed that deprotonation preferentially occurs close to an occupied *A* site, so that deprotonation is faster in amphibole compositions with fully occupied *A* sites (Susta et al. 2016; Della Ventura et al. 2017 and work in progress).

Total coefficient and calculation procedure

In the previous section, we have stressed that the application of equation 2 is biased by the errors of EMP analysis (Fig. 1). In order to overcome this problem, we first used equations 2 and 3 to calculate a preliminary formula for the high-quality amphibole data imposing total element oxides of 100 (normalized compositions), 98.2 and 101.8 wt% (deviated compositions). The resulting TC values are 1 for normalized compositions, < 1 for overestimated compositions and > 1 for underestimated compositions. Fe_2O_3 and FeO concentrations, $O^{F,Cl}$, and $\Delta charge$ can also be calculated from these preliminary unit formula. Multivariate least-square analysis on these 342 (114 x 3) data provided the following equation to be used to calculate total coefficient (TC):

$$TC = -7.9 * 10^{-4} SiO_2 + 6 * 10^{-4} TiO_2 - 6.6 * 10^{-4} Al_2O_3 + 8.75 * 10^{-5} Fe_2O_3 - 9.4 * 10^{-4} FeO -$$

$$8.5 * 10^{-4} MgO - 1.1 * 10^{-3} CaO - 1.48 * 10^{-3} Na_2O - 8.6 * 10^{-4} K_2O - 9.62 * 10^{-3} O^{F,Cl} +$$

$$6.41 * 10^{-3} H_2O - 9.57 * 10^{-3} Total\ element\ oxides + 4.13 * 10^{-4} \Delta charge + 2.024 \qquad (5)$$

where SiO_2 to K_2O are original or deviated element oxides (wt%). The calculate regression parameters are $R^2 = 0.992$ and $\sigma_{est} = 0.001$.

If the TC values are applied to the original wt% concentrations, the resulting adjusted compositions closely approach the normalized wt% concentrations of the element oxides. These adjusted compositions can then be used to obtain amphibole formulae using again equations (2) and (3). This second stage of calculations for the 114 amphiboles in our high-quality dataset produces a statistic error (σ_{est}) for the total cation sum of 0.055 apfu. The resulting formulae can be adjusted further using a series of constrains valid for Li-free and Mn-poor amphiboles (Hawthorne et al. 2012) as follows:

i) $Si \leq 8$ apfu;

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ii)   Si + Al + Ti ≥ 8 apfu;

iii)   (Si + Ti + Al + Cr + Fe$_{tot}$ + Mn + Ni + Zn + Mg) ≥ 13 apfu;

iv) $15 \leq$ total cations (i.e. $\sum_{A}^{T} apfu$) ≤ 16;

v) $46 + {}^{W}O^{2-} \geq$ charges due to all the cations, with Fe$_{tot}$ (total iron) charge equal to 2^{+}.

When applying the constraints reported above to the apfu calculated from the high-quality amphibole compositions, only sporadic and very minor adjustments involving constraint (iv) are observed (a few calculated formulae indicate total cations slightly higher than 16). In the dataset, the re-calculated total element oxides span from 99.6 to 100.5 wt%, and the final σ$_{est}$ values for the total cations and Si contents are 0.042 and 0.017 apfu, respectively. The amount of Fe^{3+} (and Fe^{2+}) can then be calculated by charge balance (eq. 4c). The $^{W}O^{2-}$, Fe^{3+} and Fe^{2+} contents can be independently estimated using the system of two linear equations (i.e. 4a and 4c):

- $^{W}O^{2-} = 4/3\,^{C}Ti + 2/3\,Fe^{3+} + 2/3\,^{A}(Na+K) - 2/3$

- $4(Si+Ti) + 3(Al+Cr+Fe^{3+}) + 2(Mg+Fe_{tot}-Fe^{3+}+Mn+Ni+Zn+Ca) + Na+K = 46 + {}^{W}O^{2-}$

The condition expressed in the constraint 4b should be respected and the priority in adjusting $^{W}O^{2-}$ and Fe^{3+} values should be given to charge balance (i.e. eq. 4c) considering that *Δcharge* can be as high as 0.1 due to error propagation in the solutions of this system.

The final formulae are used to calculate the molecular mass, M_r^F ($\sum_{A}^{W} apfu \times A_r$). M_r^F should closely approach the molecular mass calculated with equation 1 (i.e. $M_r^{CR} = 10^3 CR$) using the *CR* value obtained after the application of equation 1 to the adjusted compositions (see above). In our database, deviation percentages among these molecular masses ($\Delta MM\% = 200\frac{M_r^F - M_r^{CR}}{M_r^F + M_r^{CR}}$) range between -0.60 and 0.74%.

A step by step procedure to calculate amphibole unit-formulae is reported in a flowchart attached to this article as supplementary material. The whole procedure is included in a user-friendly Excel

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spreadsheet (also provided as supplementary material) called AMFORM. By default, this spreadsheet gives the $^WO^{2-}$ and Fe^{3+} values calculated according to equations 3 and 4c, but it also allows the use of the optional method (eq. 4a-c). We strongly recommend the use of this spreadsheet to avoid errors due to typing or unavoidable approximations of the coefficients reported in this article.

AMFORM also provides warnings for bad analyses and deviations from the correct stoichiometry such as recalculated initial totals < 98.2 and > 101.8 wt%, sum of C and B cations < 5 and 2 apfu, respectively (i.e. negative ΔC and ΔB) and $\Delta MM\% < -0.60$ and $> 0.74\%$.

Testing the AMFORM approach

To allow for an independent validation of the AMFORM approach, a test was made using additional 41 amphibole compositions belonging to the Ca, Na-Ca, Na and oxo groups, taken from the literature (King et al. 2000; Tiepolo et al. 2001; Oberti et al. 2000, 2003, 2010, 2015, 2016, 2017; Uvarova et al. 2007; Satoh et al. 2004; Della Ventura et al. 2014; Gentili et al. 2015; Gatta et al. 2017) or still unpublished (CNR-Pavia), which have been analyzed with EMP±SREF±SIMS and other techniques for Fe^{3+}/Fe_{tot} measurements (see above). It is worth noting that these amphiboles generally have higher uncertainties (e.g. total element oxides of 97-102 wt%; ΔC from -0.07 to 0.01 apfu; $\Delta charge$ from -0.09 to 0.07) than those selected for the calibration of the AMFORM procedure (see the attached AMFORM spreadsheet for these test lower-quality data).

Table 2 and Figure 4 compare the capability of AMFORM to estimate the cation and anion contents in both high-quality (calibration, blue diamonds) and lower-quality (test, yellow triangles) analyses. The generally higher $\Delta MM\%$ values of the test data suggest that this parameter is useful in warning of large analytical EMP errors (Table 2). The reliability of AMFORM is further confirmed by the homogeneous distribution around the 1:1 line of the lower-quality analyses and the absence of

outliers (Fig. 4). The few Li-free Na amphibole used to test AMFORM suggest that the method is reliable also in the case of Na amphiboles (e.g. Fig. 4c), for which the calibration is based solely on end-member compositions (Table 1; Fig. 1b).

A comparison between the AMFORM and the Locock (2014) spreadsheets

The parameters most difficult to quantify in the calculation of the amphibole unit-formula are the ^{C}Al and the ^{C}Fe^{3+}contents and the number of A cations, ^{A}(Ca + Na + K) (e.g. Leake et al. 1997; Al´meev et al. 2002; Ridolfi et al. 2010). In Figure 5, we compare the results obtained for these parameters with AMFORM to those calculated by the spreadsheet proposed by Locock (2014), which is based on the procedures suggested in the IMA 2012 classification scheme (Hawthorne et al. 2012). When the Fe^{3+}/Fe$_{tot}$ ratio, and/or the H$_2$O and Li contents are unknown (i.e., when only EMP analyses are available), the Locock (2014) spreadsheet provides two automatic procedures, depending on the presence or absence of ^{W}O^{2-}. The Fe^{3+} contents resulting from AMFORM are those of the default ^{W}O^{2-} method (eq. 3 and 4c).

Considering the unit formulae of the high-quality amphibole compositions as reference data (i.e. cation contents that for their high-quality better approach the effective unit formulae), the errors of the AMFORM procedure are, on average, 2 to 4 times lower that those obtained with the spreadsheet proposed by Locock (2014) (Fig. 5).

Locock (2014) tends to underestimate ^{C}Al and ^{A}(Ca + Na + K) in reference amphiboles with total cation contents close to 16 apfu, and slightly overestimates the same parameters when the total cation content is close to 15 apfu. Concerning the estimation of the Fe^{3+} content, Locock (2014) methods with and without ^{W}O^{2-} estimates, behaves similarly to the 13- and 15-cations methods by IMA-1997 (Leake et al. 1997) as they generally produces either large overestimations and or large underestimations, respectively (Fig. 5).

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For an independent validation of the AMFORM approach, we tested a subset of 13 published compositions of poorly-oxidized amphiboles for which Fe^{3+} had been measured by Synchroton X-ray Fluorescence (SXRF; King et al. 2000), $KMnO_4$ titration (Satoh et al. 2004) or X-ray Absorption Near Edge Structure (XANES) spectroscopy (Bonadiman et al. 2014). These data had not been included in our high-quality dataset either because they had not been examined by SREF or because they had high *Δcharge* values (up to ±0.13; see the attached AMFORM spreadsheet for these test data). When their reference Fe^{3+} values are compared to those obtained by AMFORM (yellow squares in Fig. 5c), they approach the 1:1 line and have deviations (from -0.14 to +0.16 apfu) well within the maximum-minimum error range of the AMFORM procedure.

An evaluation of the two methods used by AMFORM to calculate $^WO^{2-}$ and Fe^{3+}

Figure 6 reports plots and statistics obtained by using the default (eq. 3, 4c) and the optional (eq. 4a-c) methods to calculate the $^WO^{2-}$ and Fe^{3+} contents for 127 amphibole compositions (the 114 high-quality compositions used for calibration and the 13 lower-quality compositions where Fe^{3+}/Fe_{tot} values were measured as discussed in the previous paragraph and in Figure 5c).

The default method in AMFORM is particularly useful to estimate the amount of $^WO^{2-}$ and Fe^{3+} in poorly-oxidized amphiboles, those in equilibrium with the melt and/or other minerals. Indeed, these amphiboles are very close to (and distributed homogeneously around) the 1:1 line in Figures 6a,b and their $^WO^{2-}$ and Fe^{3+} contents can be estimated with a reasonably low uncertainty (±0.1 apfu; see Figs. 2a and 4c). In contrast, in the case of highly-oxidized amphiboles, i.e. those which underwent hydrothermal and post-crystallization oxidation, the default method may provide significant underestimation (up to 1.2 apfu, $\sigma_{est} = 0.5$ apfu; Fig. 6a,b) and therefore cannot be used to study metasomatic and oxidation processes during magma ascent (Dyar et al. 1993; King et al. 1999; Popp et al. 2006; Oberti et al. 2007a). Hence, we suggest to use the optional method for these amphiboles, because it provides a roughly homogeneous distribution around the 1:1 line in the plots in Figures 6c,d.

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The larger uncertainties in estimating $^WO^{2-}$ and Fe^{3+} values (up to 1.2 apfu, σ_{est} = 0.3 apfu) by this method are due to the large and unavoidable error propagation in the system of two linear equations (eq. 4a and 4c) and variables ($^WO^{2-}$ and Fe^{3+}).

Final remarks and recommendations

Figures 4 and Table 2 demonstrate the ability of the AMFORM approach to quantify, based solely on EMP data, the most critical parameters in the unit formula of amphiboles with a satisfactory reliability. It is worth noting that the proposed approach has been calibrated and is consistent with crystal-chemical formulae obtained by combining high-quality structure refinement and analytical data.

The AMFORM procedure has been calibrated and validated for petrologically-relevant $C2/m$ amphibole compositions (oxo, Ca, Na-Ca, and Na amphiboles, considering only Li- and Mn-free end-member compositions). The presence of significant Li and Cl contents would strongly affect the results because their lower cation mass and higher anion mass, respectively, can largely affect the behavior of the *CR-cmpg* relationship. Indeed, AMFORM should be applied only to amphiboles with Cl < 0.2 apfu (~1 wt%), Also, AMFORM only accounts for Mn^{2+} and hence cannot be used to constrain the formula of Mn^{3+}-rich amphiboles (e.g. dellaventuraite, ungarettiite; e.g. Hawthorne et al. 1995; Hawthorne et al. 2012).

However, AMFORM automatically provides warnings anytime the composition proposed deviates too much from the calibration dataset and the calculated total element oxides (both initial and adjusted) deviate too much from those of the calibration amphiboles.

The default procedure to estimate $^WO^{2-}$ and Fe^{3+} contents is particularly recommended for stability and thermobarometric studies aiming at constraining the magma pre-eruptive conditions and storage from the amphibole composition of volcanic rocks. For this purpose, the inability of estimating

the Fe^{3+} content related to hydrothermal or post-magmatic oxidizing processes may even be considered as an advantage (Ridolfi et al. 2010; Ridolfi and Renzulli 2012; Ridolfi et al. 2016). In any case, this Fe^{3+} component can be roughly estimated using the optional $^{W}O^{2-}$ and Fe^{3+} results in AMFORM.xlsx.

The mass-based method proposed in this work may open a new perspective in the calculation of the unit formula of other minerals, and is particularly useful for OH-bearing phases characterized by structural vacancies, where the total number of cation is not known. While equation 1 is valid for any type of chemical compound and mineral, equation 2 must be adapted to other phases with different proportions of anion and cation sites in order to allow a reliable estimate of *CR*, and thus, of the total cation contents.

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Table captions

Table 1.

Formula and ideal composition (wt%) of the selected Li- and Mn-free monoclinic amphibole end-members and the oxo counterparts for the Ca amphiboles considered in this work. The end-embers are ordered by increasing *Mr*. Values of *cmpg* are also reported for comparison.

Table 2.

Statistic errors of the AMFORM procedure calculated for the compositions used for calibration and for those used in the test. See AMFORM for references and data.

Figure captions

Figure 1.

Plots of CR vs. (a) M_r, molecular mass, and (b) *cmpg*, cation mass per gram. The equations (and their statistic values) obtained using normalized and end-member (Table 1) compositions are also reported. Because of EMP analytical errors, the original amphibole compositions show total element oxides varying from 98.3 to 100.8 wt%. Underestimated (< 100 wt%) and overestimated (> 100 wt%) compositions are located above and below the ideal relations, respectively. See the text for further detail.

Figure 2.

(a) Correlation between the measured (reference) $^WO^{2-}$ values and those calculated with equation 3 for 87 amphiboles with $^WO^{2-} \leq 2^CTi$ (i.e. poorly-oxidized amphiboles); the 1:1 line is reported together with the standard (σ_{est}) and maximum (Max) errors. (b) best correlation found between the reference

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$^W O^{2-}$ values and cation composition for all the 114 high-quality amphibole compositions. The red broken lines describe the proposed relation; related equations and statistic errors are also reported in red. See text for further detail.

Figure 3.

The correlation between *TC* (totals coefficient) values and those calculated with equation 5 for the 342 corrected compositions (either normalized or deviated) and the 114 original compositions. Wt% in bold indicate the normalized and deviated total element oxides; maximum and minimum uncertainties are +0.005 and -0.004.

Figure 4.

The correlation between the reference $^T Si$ (a), $^C Al$ (b), $^B Na$ (c) and $^A(Ca + Na + K)$ (d) values and those calculated with the AMFORM spreadsheet for the amphibole compositions used to calibrate the procedure (blue diamonds) and for those used for testing (yellow triangles). The 1:1 lines are reported in all diagrams (see Table 2 for statistics).

Figure 5.

The correlation between the reference $^C Al$, $^A(Ca + Na + K)$ and $^C Fe^{3+}$ values (from EMP+SREF±SIMS data) and those solely calculated from the high-quality EMP analysis in our dataset; (a-c): AMFORM; (d-f): Locock (2014) without $^W O^{2-}$ estimates; (g-i): Locock (2014) with $^W O^{2-}$ estimates. Symbols as in Fig. 2a. The statistics in diagrams (c), (f), (i) for Fe^{3+} refer to the 87 amphiboles with $^W O^{2-} \leq 2^C Ti$, whereas those in diagrams (a), (d), (g) for $^C Al$ and (b), (e), (h) for $^A(Ca + Na + K)$ refer to all the 114 amphiboles in the dataset; max and min errors are the maximum and minimum (calculated – reference) values. The orange empty squares in (c), (f), (i) represent highly-oxidized amphiboles with $^W O^{2-} > 2^C Ti$; diagram (c) also includes some amphiboles taken from the literature with $^W O^{2-} \leq 2^C Ti$, the

Fe^{3+}/Fe$_{tot}$ value of which was measured using independent techniques (yellow squares; King et al.

2000; Satoh et al. 2004; Bonadiman et al. 2014). The 1:1 line is reported in all diagrams.

Figure 6.

Correlations between the reference ^{W}O^{2-} and Fe^{3+} values and those calculated with the default (a-b) and

the optional (c-d) procedures in AMFORM for the 114 compositions used for calibration and the 13

compositions with Fe^{3+} measured by independent techniques. In (a) and (b), statistics refer only to

highly-oxidized Ca amphiboles (with ^{W}O^{2-} > ^{C}Ti) and ferri-kaersutites (symbols have the same color of

statistic values); see Fig. 2a and 4c for symbols and the statistics of poorly-oxidized amphiboles. In (c)

and (d) statistics refer to all the 127 amphiboles considered.

Figure 1   Click here to download Figure Fig. 1.pptx ☁

Fig 1.

Figure 2   Click here to download Figure Fig. 2.pptx ⬇

Fig 2.

Figure 3

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Fig 3.

Figure 4

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Fig 4.

Figure 5   Click here to download Figure Fig. 5.pptx ☑

Fig 5.

Figure 6

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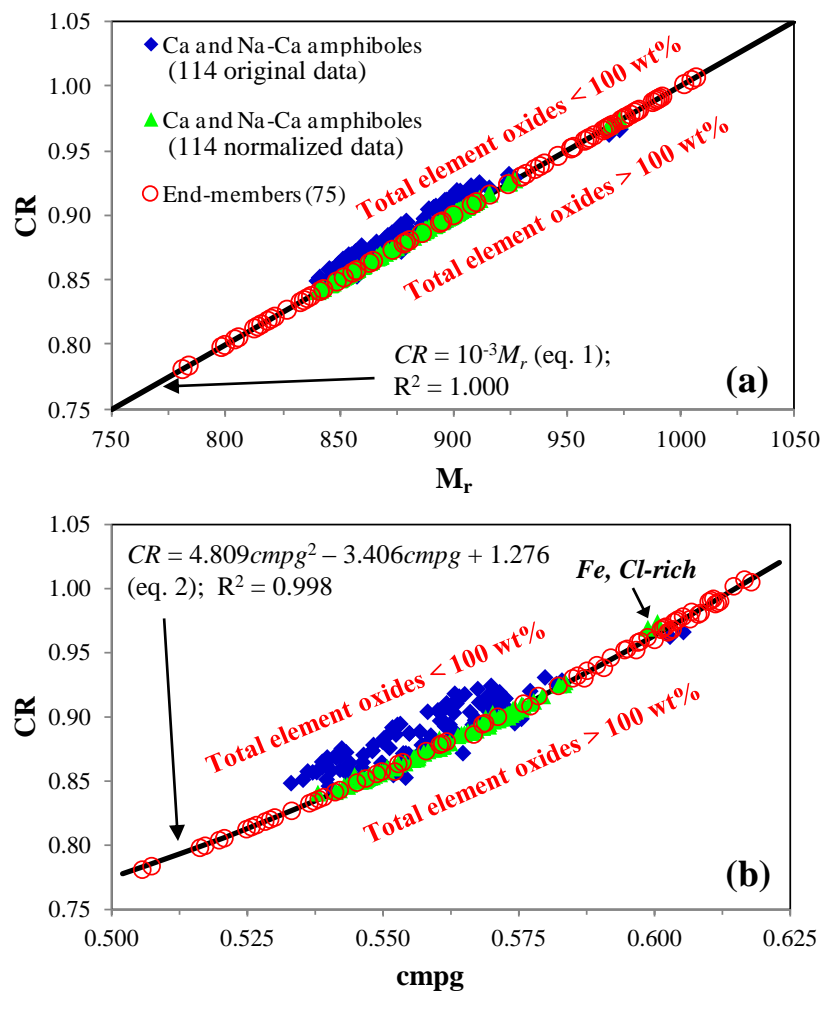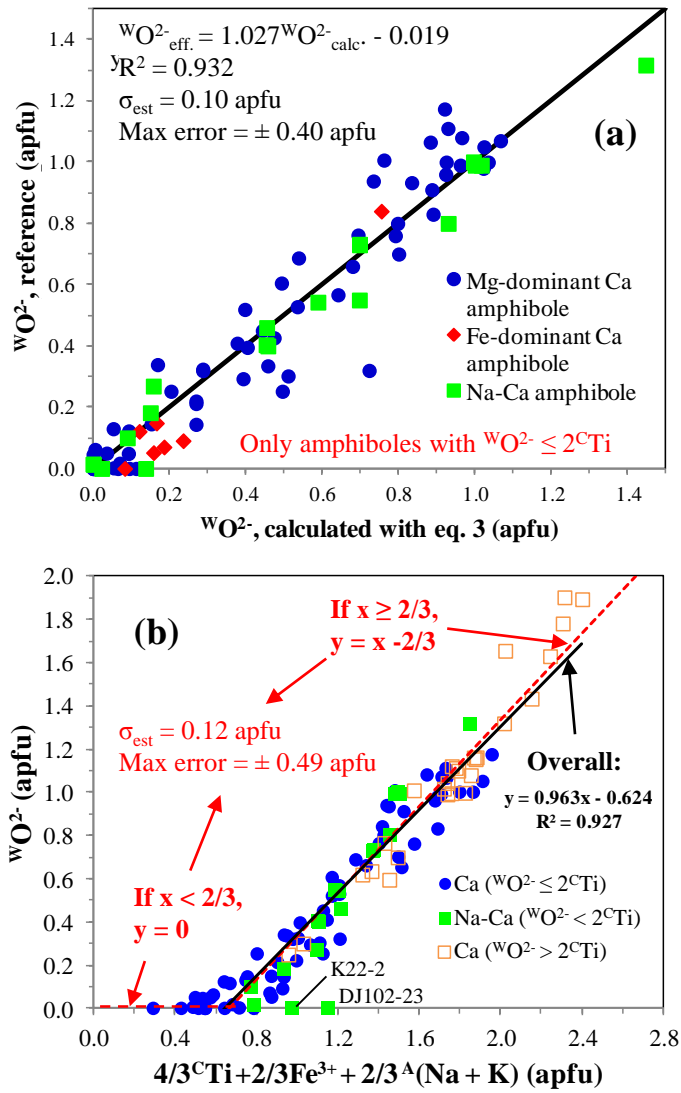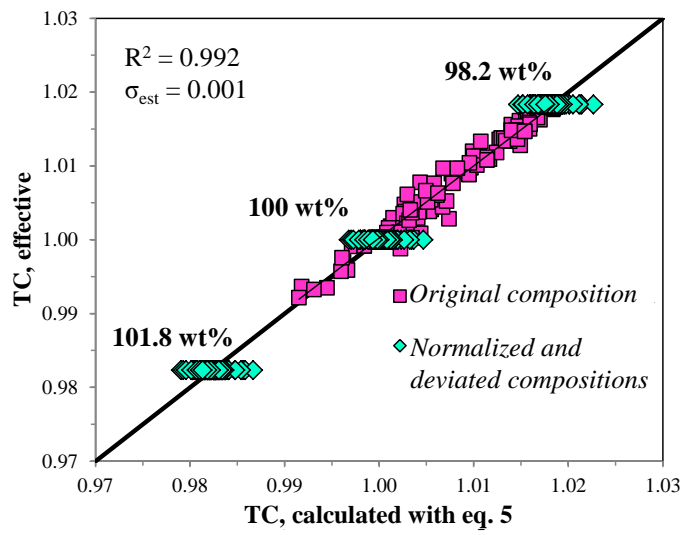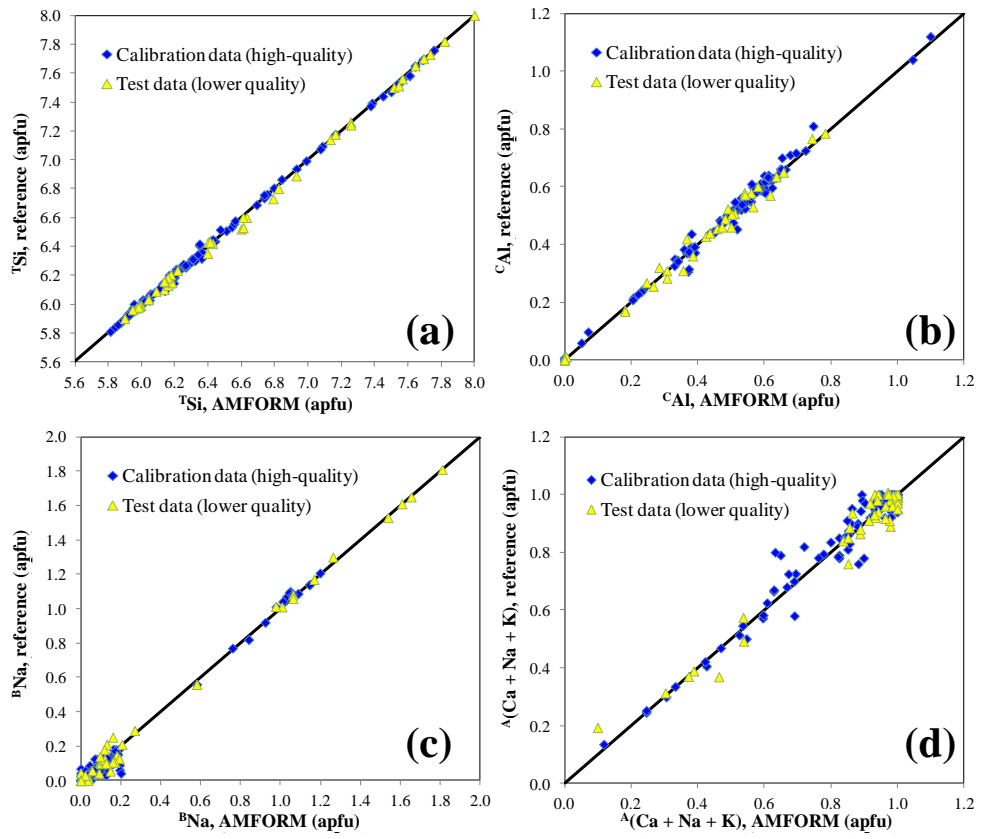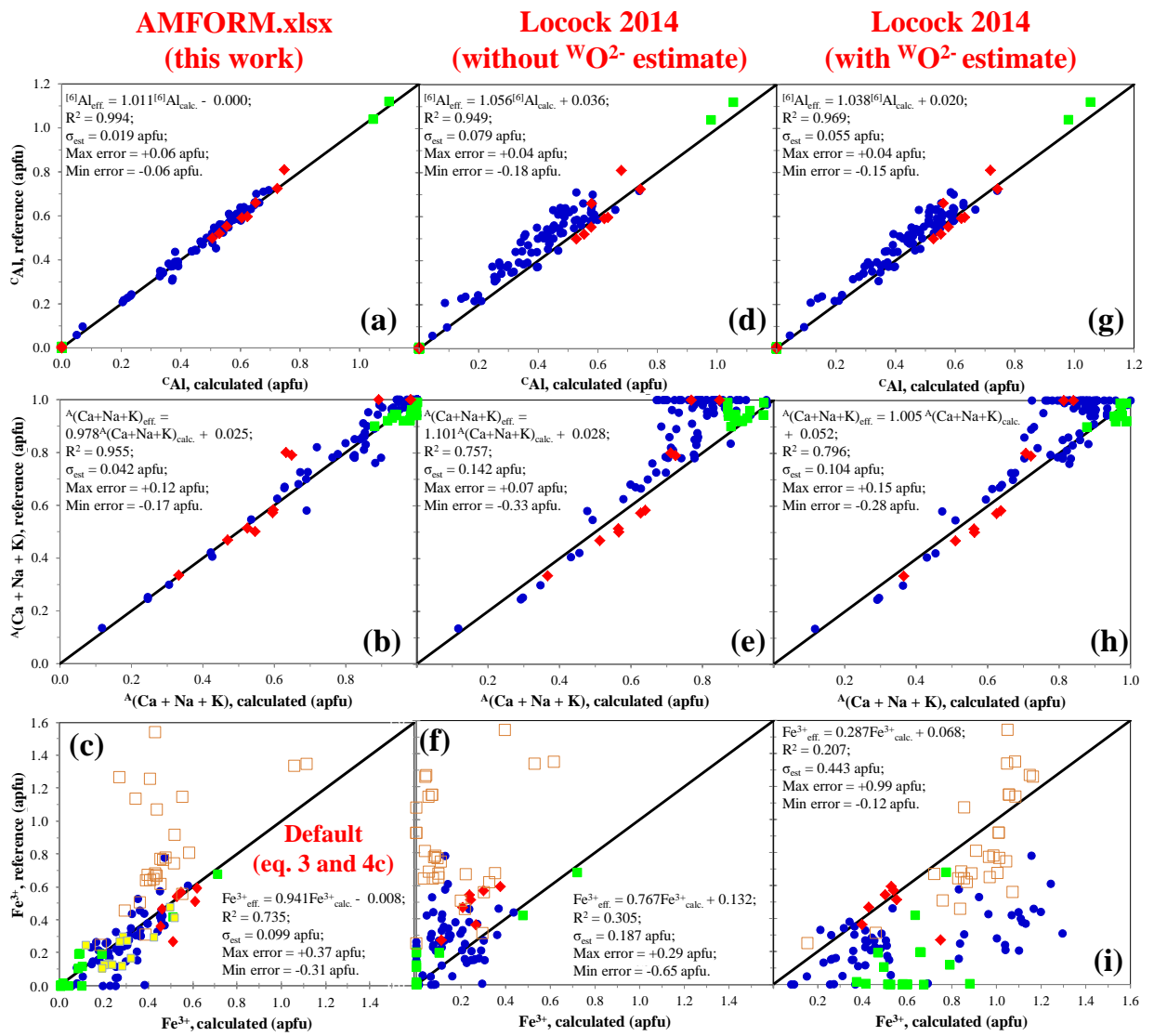
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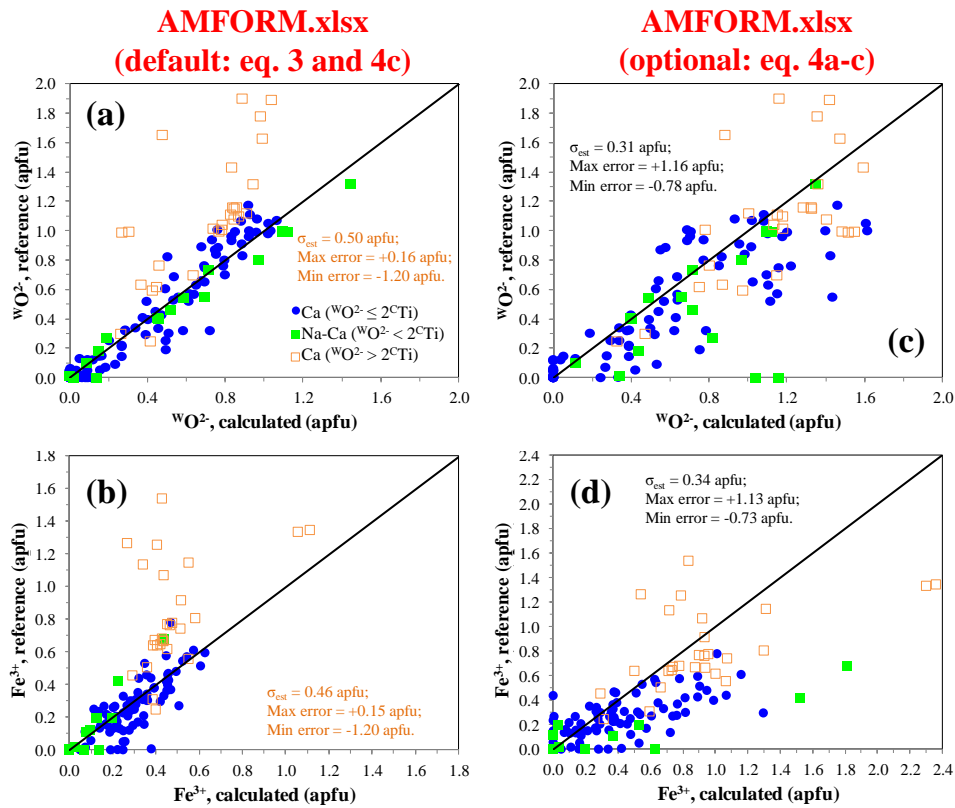
Table 1

Table 1.

Name	Group	Sub-group	Formula	SiO_2	TiO_2	Al_2O_3	FeO_{tot}	MgO	CaO	Na_2O	Sum	Fe_2O_3	FeO	H_2O	M_r	cmpg
Cummingtonite	^{W}(OH,F,Cl) Mg-Fe-Mn		$\square Mg_2Mg_5Si_8O_{22}(OH)_2$	61.56	0.00	0.00	0.00	36.13	0.00	0.00	97.69			2.31	781	0.506
Glaucophane	^{W}(OH,F,Cl) Na		$\square Na_2(Mg_3Al_2)Si_8O_{22}(OH)_2$	61.35	0.00	13.01	0.00	15.43	0.00	7.91	97.70			2.30	784	0.507
Winchite	^{W}(OH,F,Cl) Na-Ca		$\square(NaCa)(Mg_4Al)Si_8O_{22}(OH)_2$	60.24	0.00	6.39	0.00	20.20	7.03	3.88	97.74			2.26	798	0.516
Barroisite	^{W}(OH,F,Cl) Na-Ca		$\square(NaCa)(Mg_3Al_2)(Si_7Al)O_{22}(OH)_2$	52.60	0.00	19.13	0.00	15.12	7.01	3.88	97.75			2.25	800	0.517
Eckermannite	^{W}(OH,F,Cl) Na		$NaNa_2(Mg_4Al)Si_8O_{22}(OH)_2$	59.80	0.00	6.34	0.00	20.06	0.00	11.57	97.76			2.24	804	0.520
Nybøite	^{W}(OH,F,Cl) Na		$NaNa_2(Mg_3Al_2)(Si_7Al)O_{22}(OH)_2$	52.22	0.00	18.99	0.00	15.01	0.00	11.54	97.76			2.24	805	0.521
Tremolite	^{W}(OH,F,Cl) Ca		$\square Ca_2Mg_5Si_8O_{22}(OH)_2$	59.17	0.00	0.00	0.00	24.81	13.81	0.00	97.78			2.22	812	0.525
Magnesio-hornblende	^{W}(OH,F,Cl) Ca		$\square Ca_2(Mg_4Al)(Si_7Al)O_{22}(OH)_2$	51.67	0.00	12.53	0.00	19.81	13.78	0.00	97.79			2.21	814	0.526
Tschermakite	^{W}(OH,F,Cl) Ca		$\square Ca_2(Mg_3Al_2)(Si_6Al_2)O_{22}(OH)_2$	44.21	0.00	25.01	0.00	14.83	13.75	0.00	97.79			2.21	815	0.527
Richterite	^{W}(OH,F,Cl) Na-Ca		$Na(NaCa)Mg_5Si_8O_{22}(OH)_2$	58.74	0.00	0.00	0.00	24.63	6.85	7.57	97.80			2.20	818	0.528
Katophorite	^{W}(OH,F,Cl) Na-Ca		$Na(NaCa)(Mg_4Al)(Si_7Al)O_{22}(OH)_2$	51.30	0.00	12.44	0.00	19.66	6.84	7.56	97.80			2.20	820	0.529
Taramite	^{W}(OH,F,Cl) Na-Ca		$Na(NaCa)(Mg_3Al_2)(Si_6Al_2)O_{22}(OH)_2$	43.89	0.00	24.83	0.00	14.72	6.83	7.55	97.81			2.19	821	0.530
Ferri-winchite	^{W}(OH,F,Cl) Na-Ca		$\square(NaCa)(Mg_4Fe^{3+})Si_8O_{22}(OH)_2$	58.14	0.00	0.00	8.69	19.50	6.78	3.75	96.85	9.66	0.00	2.18	827	0.533
Magnesio-arfvedsonite	^{W}(OH,F,Cl) Na		$NaNa_2(Mg_4Fe^{3+})Si_8O_{22}(OH)_2$	57.72	0.00	0.00	8.63	19.36	0.00	11.16	96.88	9.59	0.00	2.16	833	0.536
Edenite	^{W}(OH,F,Cl) Ca		$NaCa_2Mg_5(Si_7Al)O_{22}(OH)_2$	50.41	0.00	6.11	0.00	24.16	13.44	3.71	97.84			2.16	834	0.537
Pargasite	^{W}(OH,F,Cl) Ca		$NaCa_2(Mg_4Al)(Si_6Al_2)O_{22}(OH)_2$	43.13	0.00	18.30	0.00	19.29	13.42	3.71	97.84			2.16	836	0.538
Sadanagaite	^{W}(OH,F,Cl) Ca		$NaCa_2(Mg_3Al_2)(Si_5Al_3)O_{22}(OH)_2$	35.88	0.00	30.44	0.00	14.44	13.39	3.70	97.85			2.15	837	0.539
Magnesio-riebeckite	^{W}(OH,F,Cl) Na		$\square Na_2(Mg_3Fe^{3+}_2)Si_8O_{22}(OH)_2$	57.14	0.00	0.00	17.08	14.37	0.00	7.37	95.96	18.98	0.00	2.14	841	0.541
Magnesio-ferri-hornblende	^{W}(OH,F,Cl) Ca		$\square Ca_2(Mg_4Fe^{3+})(Si_7Al)O_{22}(OH)_2$	49.90	0.00	6.05	8.52	19.13	13.31	0.00	96.91	9.47	0.00	2.14	843	0.542
Ferri-katophorite	^{W}(OH,F,Cl) Na-Ca		$Na(NaCa)(Mg_4Fe^{3+})(Si_7Al)O_{22}(OH)_2$	49.56	0.00	6.01	8.47	19.00	6.61	7.30	96.93	9.41	0.00	2.12	849	0.545
Cannilloite	^{W}(OH,F,Cl) Ca		$CaCa_2(Mg_4Al)(Si_5Al_3)O_{22}(OH)_2$	35.27	0.00	23.94	0.00	18.93	19.75	0.00	97.89			2.11	852	0.547
Rootname 4	^{W}(OH,F,Cl) Ca		$NaCa_2(Mg_3Ti)(Si_5Al_3)O_{22}(OH)_2$	35.11	9.33	17.88	0.00	18.84	13.11	3.62	97.89			2.11	856	0.549
Kaersutite	^{W}O -		$NaCa_2(Mg_3TiAl)(Si_6Al_2)O_{22}O_2$	42.05	9.32	17.84	0.00	14.10	13.08	3.61	100.00			0.00	857	0.552
Ferri-barroisite	^{W}(OH,F,Cl) Na-Ca		$Na(NaCa)(Mg_3Fe^{3+}_2)(Si_7Al)O_{22}(OH)_2$	49.06	0.00	5.95	16.76	14.10	6.54	3.61	96.03	18.63	0.00	2.10	857	0.550
Ferri-nybøite	^{W}(OH,F,Cl) Na		$NaNa_2(Mg_3Fe^{3+}_2)(Si_7Al)O_{22}(OH)_2$	48.73	0.00	5.91	16.65	14.01	0.00	10.77	96.06	18.50	0.00	2.09	863	0.553
Magnesio-hastingsite	^{W}(OH,F,Cl) Ca		$NaCa_2(Mg_4Fe^{3+})(Si_6Al_2)O_{22}(OH)_2$	41.69	0.00	11.79	8.31	18.64	12.97	3.58	96.99	9.23	0.00	2.08	865	0.554
Ferri-tschermakite	^{W}(OH,F,Cl) Ca		$\square Ca_2(Mg_3Fe^{3+}_2)(Si_6Al_2)O_{22}(OH)_2$	41.28	0.00	11.68	16.45	13.85	12.84	0.00	96.10	18.29	0.00	2.06	873	0.558
Ferro-glaucophane	^{W}(OH,F,Cl) Na		$\square Na_2(Fe^{2+}_3Al_2)Si_8O_{22}(OH)_2$	54.74	0.00	11.61	24.54	0.00	0.00	7.06	97.95	0.00	24.54	2.05	878	0.560
Ferri-taramite	^{W}(OH,F,Cl) Na-Ca		$Na(NaCa)(Mg_3Fe3+_2)(Si_6Al_2)O_{22}(OH)_2$	41.01	0.00	11.60	16.34	13.75	6.38	7.05	96.13	18.16	0.00	2.05	879	0.561
Ferri-cannilloite	^{W}(OH,F,Cl) Ca		$CaCa_2(Mg_4Fe^{3+})(Si_5Al_3)O_{22}(OH)_2$	34.11	0.00	17.37	8.16	18.31	19.10	0.00	97.05	9.07	0.00	2.05	881	0.562
Ferri-kaersutite	^{W}O -		$NaCa_2(Mg_3TiFe^{3+})(Si_6Al_2)O_{22}O_2$	40.68	9.01	11.51	8.11	13.64	12.66	3.50	99.10	9.01	0.00	0.00	886	0.567
Ferro-barroisite	^{W}(OH,F,Cl) Na-Ca		$\square(NaCa)(Fe^{2+}_3Al_2)(Si_7Al)O_{22}(OH)_2$	47.04	0.00	17.10	24.11	0.00	6.27	3.47	97.99	0.00	24.11	2.01	894	0.568
Ferri-sadanagaite	^{W}(OH,F,Cl) Ca		$NaCa_2(Mg_3Fe^{3+}_2)(Si_5Al_3)O_{22}(OH)_2$	33.56	0.00	17.09	16.05	13.51	12.53	3.46	96.20	17.84	0.00	2.01	895	0.569
Ferro-nybøite	^{W}(OH,F,Cl) Na		$NaNa_2(Fe^{2+}_3Al_2)(Si_7Al)O_{22}(OH)_2$	46.73	0.00	16.99	23.95	0.00	0.00	10.33	98.00	0.00	23.95	2.00	900	0.571
oxo Ferro-tschermakite	^{W}O Ca		$\square Ca_2(Fe^{2+}Fe^{3+}_2Al_2)(Si_6Al_2)O_{22}O_2$	39.70	0.00	22.46	23.73	0.00	12.35	0.00	98.24	17.58	7.91	0.00	908	0.577
Ferro-tschermakite	^{W}(OH,F,Cl) Ca		$\square Ca_2(Fe^{2+}_3Al_2)(Si_6Al_2)O_{22}(OH)_2$	39.61	0.00	22.41	23.68	0.00	12.32	0.00	98.02	0.00	23.68	1.98	910	0.576
Ferro-taramite	^{W}(OH,F,Cl) Na-Ca		$Na(NaCa)(Fe^{2+}_3Al_2)(Si_6Al_2)O_{22}(OH)_2$	39.35	0.00	22.26	23.53	0.00	6.12	6.77	98.03	0.00	23.53	1.97	916	0.579
Ferro-winchite	^{W}(OH,F,Cl) Na-Ca		$\square(NaCa)(Fe2+4Al)Si8O22(OH)2$	52.01	0.00	5.52	31.10	0.00	6.07	3.35	98.05	0.00	31.10	1.95	924	0.582
oxo Ferro-sadanagaite	^{W}O Ca		$NaCa_2(Fe^{2+}Fe^{3+}Al_2)(Si_5Al_3)O_{22}O_2$	32.30	0.00	27.41	23.18	0.00	12.06	3.33	98.28	17.17	7.73	0.00	930	0.587
Ferro-eckermannite	^{W}(OH,F,Cl) Na		$NaNa_2(Fe^{2+}_4Al)Si_8O_{22}(OH)_2$	51.68	0.00	5.48	30.90	0.00	0.00	10.00	98.06	0.00	30.90	1.94	930	0.585
Ferro-sadanagaite	^{W}(OH,F,Cl) Ca		$NaCa_2(Fe^{2+}_3Al_2)(Si_5Al_3)O_{22}(OH)_2$	32.23	0.00	27.35	23.13	0.00	12.03	3.33	98.07	0.00	23.13	1.93	932	0.586
Riebeckite	^{W}(OH,F,Cl) Na		$\square Na_2(Fe^{2+}_3Fe^{3+}_2)Si_8O_{22}(OH)_2$	51.36	0.00	0.00	38.38	0.00	0.00	6.62	96.37	17.06	23.03	1.92	936	0.588
oxo Ferro-hornblende	^{W}O Ca		$\square Ca_2(Fe^{2+}_2Fe^{3+}_2Al)(Si_7Al)O_{22}O_2$	44.83	0.00	10.87	30.63	0.00	11.96	0.00	98.29	17.02	15.32	0.00	938	0.591
Ferro-hornblende	^{W}(OH,F,Cl) Ca		$\square Ca_2(Fe^{2+}_4Al)(Si_7Al)O_{22}(OH)_2$	44.74	0.00	10.85	30.57	0.00	11.93	0.00	98.08	0.00	30.57	1.92	940	0.589
Ferro-katophorite	^{W}(OH,F,Cl) Na-Ca		$Na(NaCa)(Fe^{2+}_4Al)(Si_7Al)O_{22}(OH)_2$	44.46	0.00	10.78	30.38	0.00	5.93	6.55	98.10	0.00	30.38	1.90	946	0.592
Ferro-ferri-barroisite	^{W}(OH,F,Cl) Na-Ca		$\square(NaCa)(Fe^{2+}_3Fe^{3+}_2)(Si_7Al)O_{22}(OH)_2$	44.19	0.00	5.36	37.74	0.00	5.89	3.26	96.43	16.78	22.64	1.89	952	0.594
Ferro-kaersutite	^{W}O -		$NaCa_2(Fe^{2+}_3TiAl)(Si_6Al_2)O_{22}O_2$	37.87	8.39	16.07	22.64	0.00	11.78	3.26	100.00	0.00	22.64	0.00	952	0.597
Ferro-ferri-winchite	^{W}(OH,F,Cl) Na-Ca		$\square(NaCa)(Fe^{2+}_4Fe^{3+})Si_8O_{22}(OH)_2$	50.44	0.00	0.00	37.69	0.00	5.88	3.25	97.27	8.38	30.16	1.89	953	0.595
Ferro-ferri-nybøite	^{W}(OH,F,Cl) Na		$NaNa2(Fe2+3Fe3+2)(Si7Al)O22(OH)2$	43.91	0.00	5.32	37.51	0.00	0.00	9.71	96.45	16.67	22.50	1.88	958	0.597
Arfvedsonite	^{W}(OH,F,Cl) Na		$NaNa_2(Fe^{2+}_4Fe^{3+})Si_8O_{22}(OH)_2$	50.13	0.00	0.00	37.46	0.00	0.00	9.70	97.29	8.33	29.97	1.88	959	0.597
oxo Ferro-pargasite	^{W}O Ca		$NaCa_2(Fe^{2+}_2Fe^{3+}Al)(Si_6Al_2)O_{22}O_2$	37.55	0.00	15.93	29.94	0.00	11.68	3.23	98.33	16.63	14.97	0.00	960	0.600
Ferro-pargasite	^{W}(OH,F,Cl) Ca		$NaCa_2(Fe^{2+}_4Al)(Si_6Al_2)O_{22}(OH)_2$	37.47	0.00	15.90	29.87	0.00	11.66	3.22	98.13	0.00	29.87	1.87	962	0.599

Table 1. Continue.

Name	Group	Sub-group	Formula	SiO_2	TiO_2	Al_2O_3	FeO_{tot}	MgO	CaO	Na_2O	Sum	Fe_2O_3	FeO	H_2O	M_r	cmpg
oxo Ferro-ferri-hornblende	^{W}O	Ca	$\square Ca_2(Fe^{2+}{}_2Fe^{3+}{}_3)(Si_7Al)O_{22}O_2$	43.50	0.00	5.27	37.15	0.00	11.60	0.00	97.52	24.77	14.86	0.00	967	0.603
oxo Ferro-cannilloite	^{W}O	Ca	$CaCa_2(Fe^{2+}{}_2Fe^{3+}{}_2Al)(Si_5Al_3)O_{22}O_2$	30.78	0.00	20.89	29.45	0.00	17.24	0.00	98.36	16.36	14.72	0.00	976	0.607
oxo Ferro-ferri-tschermakite	^{W}O	Ca	$\square Ca_2(Fe^{2+}Fe^{3+}{}_4)(Si_6Al_2)O_{22}O_2$	37.33	0.00	10.56	37.19	0.00	11.61	0.00	96.69	33.07	7.44	0.00	966	0.602
Ferro-ferri-tschermakite	^{W}(OH,F,Cl)	Ca	$\square Ca_2(Fe^{2+}{}_3Fe^{3+}{}_2)(Si_6Al_2)O_{22}(OH)_2$	37.25	0.00	10.53	37.12	0.00	11.59	0.00	96.49	16.50	22.27	1.86	968	0.601
oxo Ferro-actinolite	^{W}O	Ca	$\square Ca_2(Fe^{2+}{}_3Fe^{3+}{}_2)Si_8O_{22}O_2$	49.65	0.00	0.00	37.11	0.00	11.59	0.00	98.35	16.50	22.26	0.00	968	0.603
Ferro-ferri-hornblende	^{W}(OH,F,Cl)	Ca	$\square Ca_2(Fe^{2+}{}_4Fe^{3+})(Si_7Al)O_{22}(OH)_2$	43.41	0.00	5.26	37.07	0.00	11.57	0.00	97.32	8.24	29.66	1.86	969	0.602
Ferro-actinolite	^{W}(OH,F,Cl)	Ca	$\square Ca_2Fe^{2+}{}_5Si_8O_{22}(OH)_2$	49.55	0.00	0.00	37.03	0.00	11.56	0.00	98.14	0.00	37.03	1.86	970	0.602
Ferro-ferri-taramite	^{W}(OH,F,Cl)	Na-Ca	$Na(NaCa)(Fe^{2+}{}_3Fe^{3+}{}_2)(Si_6Al_2)O_{22}(OH)_2$	37.02	0.00	10.47	36.89	0.00	5.76	6.36	96.51	16.40	22.13	1.85	974	0.604
Ferro-ferri-katophorite	^{W}(OH,F,Cl)	Na-Ca	$Na(NaCa)(Fe^{2+}{}_4Fe^{3+})(Si_7Al)O_{22}(OH)_2$	43.14	0.00	5.23	36.85	0.00	5.75	6.36	97.33	8.19	29.48	1.85	975	0.604
Ferro-richterite	^{W}(OH,F,Cl)	Na-Ca	$Na(NaCa)Fe^{2+}{}_5Si8O_{22}(OH)_2$	49.25	0.00	0.00	36.81	0.00	5.75	6.35	98.15	0.00	36.81	1.85	976	0.604
Ferro-cannilloite	^{W}(OH,F,Cl)	Ca	$CaCa_2(Fe^{2+}{}_4Al)(Si_5Al_3)O_{22}(OH)_2$	30.72	0.00	20.85	29.39	0.00	17.20	0.00	98.16	0.00	29.39	1.84	978	0.605
oxo Ferro-rootname 4	^{W}O	Ca	$NaCa_2(Fe^{2+}{}_2Fe^{3+}{}_2Ti)(Si_5Al_3)O_{22}O_2$	30.66	8.15	15.61	29.33	0.00	11.45	3.16	98.37	16.30	14.67	0.00	980	0.608
Ferro-ferri-kaersutite	^{W}O	-	$NaCa_2(Fe^{2+}{}_3TiFe^{3+})(Si_6Al_2)O_{22}O_2$	36.75	8.14	10.40	29.30	0.00	11.43	3.16	99.18	8.14	21.97	0.00	981	0.609
Ferro-rootname 4	^{W}(OH,F,Cl)	Ca	$NaCa_2(Fe^{2+}{}_4Ti)(Si_5Al_3)O_{22}(OH)_2$	30.60	8.13	15.58	29.27	0.00	11.42	3.16	98.17	0.00	29.27	1.83	982	0.607
oxo Ferro-ferri-sadanagaite	^{W}O	Ca	$NaCa_2(Fe^{2+}{}_2Fe^{3+}{}_3)(Si_5Al_3)O_{22}O_2$	30.42	0.00	15.48	36.37	0.00	11.35	3.14	96.76	32.33	7.27	0.00	988	0.611
oxo Hastingsite	^{W}O	Ca	$NaCa_2(Fe^{2+}{}_2Fe^{3+}{}_3)(Si_6Al_2)O_{22}O_2$	36.46	0.00	10.31	36.33	0.00	11.34	3.13	97.57	24.22	14.53	0.00	989	0.612
Ferro-ferri-sadanagaite	^{W}(OH,F,Cl)	Ca	$NaCa_2(Fe^{2+}{}_3Fe^{3+}{}_2)(Si_5Al_3)O_{22}(OH)_2$	30.35	0.00	15.45	36.29	0.00	11.33	3.13	96.56	16.13	21.78	1.82	990	0.610
oxo Ferro-edenite	^{W}O	Ca	$NaCa_2(Fe^{2+}{}_3Fe^{3+}{}_2)(Si_7Al)O_{22}O_2$	42.49	0.00	5.15	36.29	0.00	11.33	3.13	98.38	16.13	21.77	0.00	990	0.612
Hastingsite	^{W}(OH,F,Cl)	Ca	$NaCa_2(Fe^{2+}{}_4Fe^{3+})(Si_6Al_2)O_{22}(OH)_2$	36.38	0.00	10.29	36.25	0.00	11.32	3.13	97.37	8.06	29.00	1.82	991	0.610
Ferro-edenite	^{W}(OH,F,Cl)	Ca	$NaCa_2Fe^{2+}{}_5(Si_7Al)O_{22}(OH)_2$	42.40	0.00	5.14	36.21	0.00	11.31	3.12	98.18	0.00	36.21	1.82	992	0.611
Grunerite	^{W}(OH,F,Cl)	Mg-Fe-Mn	$\square Fe^{2+}{}_2Fe^{2+}{}_5Si_8O_{22}(OH)_2$	47.99	0.00	0.00	50.21	0.00	0.00	0.00	98.20	0.00	50.21	1.80	1002	0.615
oxo Ferro-ferri-cannilloite	^{W}O	Ca	$CaCa_2(Fe^{2+}{}_2Fe^{3+}{}_3)(Si_5Al_3)O_{22}O_2$	29.90	0.00	15.22	35.75	0.00	16.74	0.00	97.61	23.84	14.30	0.00	1005	0.618
Ferro-ferri-cannilloite	^{W}(OH,F,Cl)	Ca	$CaCa_2(Fe^{2+}{}_4Fe^{3+})(Si_5Al_3)O_{22}(OH)_2$	29.84	0.00	15.19	35.68	0.00	16.71	0.00	97.42	7.93	28.54	1.79	1007	0.617

Table 2

Table 2.

Amphibole parameter	Calibration high-quality data N = 114		Test lower-quality data N = 34	
	σ_{est}	max error	σ_{est}	max error
^{T}Si	0.017	0.068	0.028	0.081
^{C}Al	0.019	0.065	0.022	0.052
^{C}Ti	0.012	0.087	0.008	0.040
Fe_{T}	0.007	0.045	0.027	0.121
Mg_{T}	0.008	0.028	0.015	0.045
Ca_{T}	0.005	0.019	0.005	0.012
^{B}Na	0.036	0.159	0.036	0.093
^{A}Na	0.038	0.165	0.038	0.094
^{A}K	0.002	0.007	0.002	0.005
$^{A}(Ca + Na + K)$	0.042	0.168	0.042	0.094
F	0.004	0.016	0.015	0.060
ΔMM%	0.18	0.74	0.26	0.87

N: sample number; σ_{est}: error standard of the estimate; max error: maximum error
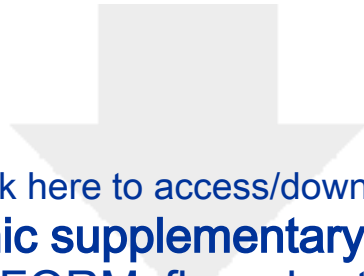
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