

## Amphibole equilibria in mantle rocks: Determining values of mantle $a_{\text{H}_2\text{O}}$ and implications for mantle $\text{H}_2\text{O}$ contents

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### APPENDIX: AMPHIBOLE NORMALIZATION

A typical amphibole formula may be written as  $\text{A}_{0-1}\text{E}_2\text{G}_5\text{T}_8\text{O}_{22}(\text{Z})_2$  (site occupancy nomenclature after Smith et al. 1998) where A = Na, K; E = Na, Li, Ca, Mn,  $\text{Fe}^{2+}$ , Mg; G = Mg,  $\text{Fe}^{2+}$ , Mn, Al,  $\text{Fe}^{3+}$ , Ti; T = Si, Al; and Z = OH, F, Cl,  $\square$  (where  $\square$  indicates an H vacancy and is equivalent to  $\text{O}^{2-}$  in the Z-site). The E site corresponds to the M4 cation site, the G site corresponds to the combined M1, M2, and M3 octahedral sites, the T-site is the tetrahedral site, and the Z site corresponds to the O3 site (Hawthorne 1981). Determining an amphibole formula from chemical information obtained via electron-microprobe analysis typically suffers from three unknowns: (1) the ratio of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ ; (2) the amount of oxy-substitution or  $\square$  (i.e., substitution of O for OH, Cl, and/or F on the Z-site); and (3) the proportion of the A-site that is vacant. Thus, complete characterization of the chemical formula of an amphibole requires a determination of ratio of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  and the H-content of the amphibole, in addition to the major- and minor-element content. Given a complete chemical analysis, as well as constraints on the site-occupancy and charge balance, it is possible to determine a formula for many amphiboles even if the A-site occupancy has not been independently determined.

In the present study, cation site occupancies in amphibole were assigned as follows. The T site must contain all the Si cations. If the total number of Si cations is  $<8$ , the remaining T sites were filled with Al. Any remaining Al, as well as all  $\text{Fe}^{3+}$  and Ti were assigned to the G sites.  $\text{Fe}^{2+}$  and Mg were assigned to the G sites until the total sum of all cations in the G sites was five (i.e., the G site is filled). If the G site is not completely filled with Al +  $\text{Fe}^{3+}$  + Ti + Mg +  $\text{Fe}^{2+}$ , then Mn was assigned to the G site to bring the cation total in this site to five. Any remaining Mn was assigned to the E site. If, on the other hand, there is excess Mg and  $\text{Fe}^{2+}$  after the G site was filled, the excess Mg +  $\text{Fe}^{2+}$  was assigned to the E site such that the ratio of Fe to Mg is the same in both the E and G sites. Ca was assigned to the E site. If the E site is not full after all the Ca has been assigned to this site, then Na was placed in the E site until the total number of cations in this site is 2. Any remaining Na was assigned to the A site, along with any K.

This procedure for assigning cations to crystallographic sites

was designed for calcic or sodic-calcic amphiboles with significant Fe-oxy content and may not accurately describe cation site populations in other amphibole varieties. In particular, in many amphiboles,  $\text{Fe}^{3+}$  and other smaller trivalent cations are largely restricted to the M2 sites. However, this is not the case for amphibole with significant oxy-component. Results from X-ray crystal structure refinements (Phillips et al. 1988) and Mössbauer spectral studies (Popp et al. 1995b) document that the M1 and M3 sites in oxy-amphiboles contain significant  $\text{Fe}^{3+}$ . Furthermore, in many amphiboles  $\text{Fe}^{2+}$  is partitioned preferentially into the M4 site as compared to the M1, M2, and M3 sites. This partitioning depends largely upon temperature and composition and, therefore, when assigning cations to sites some simplification is probably necessary. Two end-member cases are: (1) assigning all the  $\text{Fe}^{2+}$  to the M4 site, or (2) partitioning the  $\text{Fe}^{2+}$  between M4, and M1, M2, and M3 in a simple fashion (the approach taken here). The estimated activity of an amphibole end-member (e.g., pargasite), as well as the estimated values of  $a_{\text{H}_2\text{O}}$ , will depend, in part, upon the site occupancy of  $\text{Fe}^{2+}$ . The Fe in the amphibole from sample DH101E is highly oxidized and, therefore, the amount of  $\text{Fe}^{2+}$  is relatively small. Consequently, the difference in the estimated value of  $a_{\text{H}_2\text{O}}$  that arises from whether  $\text{Fe}^{2+}$  is restricted to the M4 site, or partitioned between this site and the M1, M2, and M3 sites, is also relatively small, and this difference does not effect the conclusions of this study.

A significant portion of the amphibole A-site may be vacant. Consequently, if the amount of the vacancy has not been quantified, the total number of cations that may be present in one formula unit of any given amphibole may vary from 15 to 16. If the anion occupancy of the Z site has been fully characterized, then the total negative charge is known. Given the total negative charge, it is possible to vary the total number of cations in the amphibole formula between 15 and 16, while keeping the relative proportions of these cations constant, and, therefore, vary the total positive charge until it is equivalent to the total negative charge. This approach yields an estimation of the total number of cations in the amphibole formula, such that it is possible to calculate the proportion of the A-site that is vacant.

In practice, an iterative procedure was used to calculate amphibole chemical formulae. Amphiboles were first normalized to a fixed number of O atoms, which yields more than 16 cations

pfu. At this point, the number of cations was reduced in small increments while keeping their relative proportions constant until charge balance was attained while satisfying the site-occupancy requirements. In each iteration, the cation site occupancies were recalculated, which in turn, produces a revised Z-site occupancy (see below).

The chemical formula of the amphibole from Dish Hill DH101E was normalized following the procedures outlined above. Although the ratio of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  in the amphibole had been determined, the H content has not been measured directly. However, empirically determined relations between the cation contents, the  $\text{Fe}^{3+}:\text{Fe}^{2+}$  ratio, and the H contents of amphiboles can be used to completely characterize the chemical composition of the amphibole.

Rigorous statistical analyses of the compositions of kaersutitic amphiboles from alkalic igneous rocks and mafic mantle xenoliths show that the oxy-substitution ( $\text{OH}^- \rightleftharpoons \square$ ) in these amphiboles may not be controlled by simple substitution mechanisms, and that no single mechanism may operate in all amphiboles (Young et al. 1997). Nevertheless, two different relations have been used to obtain reasonably accurate estimates of the oxy/hydroxy content of mantle amphiboles, given the major and minor element contents and the  $\text{Fe}^{3+}:\text{Fe}^{2+}$  ratio. One of these relations equates the amount of  $\text{O}^{2-}$  (i.e.,  $\square$ ) in the Z site to the sum of the  $\text{Fe}^{3+}$  and  $\text{Ti}^{4+}$  in the amphibole formula (Popp et al. 1995a) such that:

$$2.0 = \text{Fe}^{3+} + \text{Ti}^{4+} + \text{OH}^- + \text{Cl}^- + \text{F}^- \text{ (apfu)}. \quad (\text{A1})$$

Thus, Equation A1 requires that  $\square = \text{Fe}^{3+} + \text{Ti}^{4+}$  (atoms per formula unit or apfu), and defines the amount of both oxy- and hydroxy-component apfu in the Z site.

The second relation between cation content and Z-site occupancy can be derived from the relation:

$$\text{Fe}^{3+} = 2.47 - 0.93(\text{OH}) - (\text{Ti} + \text{Al}^{\text{VI}}) \text{ (apfu)} \quad (\text{A2})$$

(King et al. 1999). When Equation A2 is combined with the equation describing Z site occupancy,  $2.0 = \text{OH} + \square + \text{F} + \text{Cl}$ , the oxy- and hydroxy-component in the Z site are again both defined.

To test the accuracy of Equations A1 and A2 in predicting Z-site occupancy, the two methods were tested on amphiboles in which both the  $\text{Fe}^{3+}:\text{Fe}^{2+}$  ratio and the  $\text{H}_2\text{O}$  content had been determined, and, therefore, a comparison between the calculated and measured  $\text{H}_2\text{O}$  content is possible. The amphibole analyses used for this comparison come from three sources: (1) Dyar et al. (1993); (2) Popp et al. (2006a); and (3) those samples from King et al. (1999) in which independent values of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  were determined by Righter and Carmichael (1993). These published amphibole analyses were normalized using the procedure described above, combined with Equation A1 or A2 to fully define the Z-site occupancy of the amphibole.

The calculation of amphibole formulae using this method will, in some cases, yield an amphibole formula in which the total positive charge will not be equal to the total negative charge given the constraints on cation-site populations defined above. This lack of charge balance implies that the amphibole

analysis is less than perfect, and could result from inaccuracies involved in the determination of the amount of  $\square$  in the Z site using Equation A1 or A2, or from small uncertainties in the chemical analyses typically assigned to electron-microprobe analyses, or a combination of these two factors. In those cases where charge balance was not attained initially, the amphibole formula was determined in two different ways. First, using the same iterative procedure described previously, the difference between the positive and negative charges was minimized while still satisfying cation-site occupancies, the  $\text{H}_2\text{O}$  content was then determined from the resulting amphibole formula. Second, after this amphibole formula, with minimal charge imbalance, was determined, the  $\text{OH}^-:\text{O}^{2-}$  ratio was varied until charge balance was achieved. In this second case, the amount of  $\text{O}^{2-}$  in the Z-site was slightly inconsistent with either Equation A1 or A2. The final OH content of those amphiboles that did not initially produce a charge balance was determined by averaging the OH content derived by these two methods.

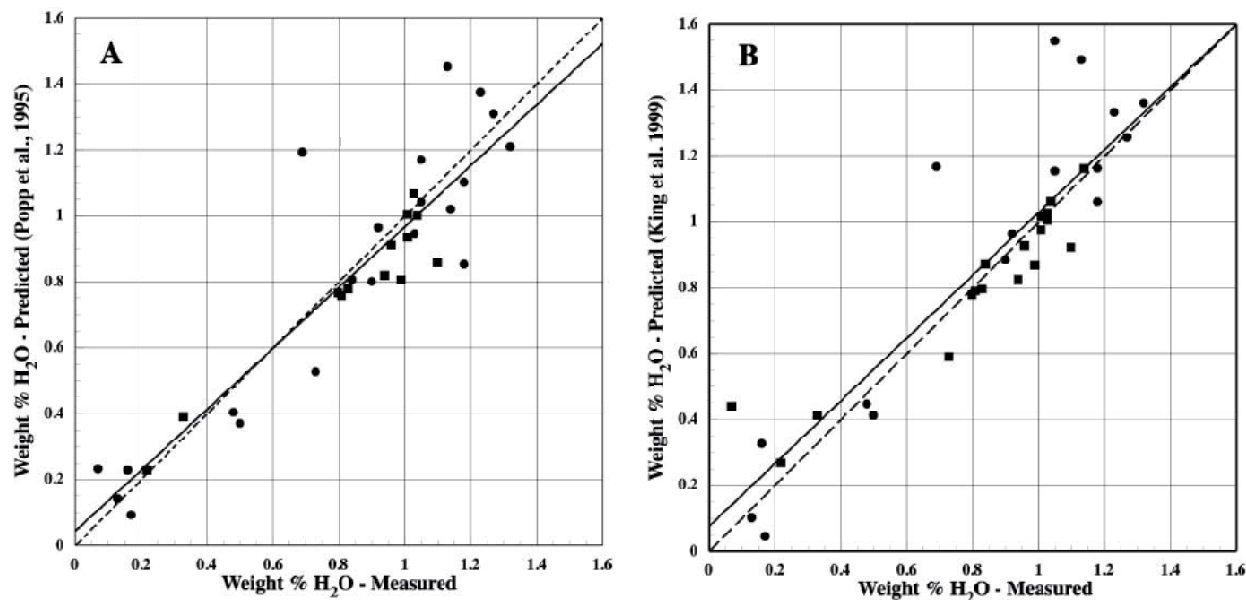
The uncertainty in the amount of  $\text{H}_2\text{O}$  in these amphiboles—as determined using the iterative procedure (described above) combined with Equation A1 or A2—that is due only to analytical uncertainty can be estimated using the procedure described in the text above (i.e., randomly generating 1000 analyses whose variation from the original analyses is based on the analytical uncertainty for each element analyzed). For sample DH101E, the result is a  $1\sigma$  deviation of  $\sim 0.015$ , or about 1.1% of the amount of  $\text{H}_2\text{O}$  in this amphibole. This value, 1.1%, is then taken to be an approximation of the effect of the analytical uncertainty on the calculated amount of  $\text{H}_2\text{O}$  for each amphibole considered here.

Figure A1a shows the  $\text{H}_2\text{O}$  content of the amphiboles, in wt%, calculated using Equation A1 (Popp et al. 1995a) to define the oxy-/hydroxy-contents, combined with the site-occupancy constraints discussed above. Figure A1b shows the results using Equation A2 (King et al. 1999) to define the oxy-/hydroxy-contents. Figure A1a shows generally good agreement between calculated and measured values of  $\text{H}_2\text{O}$ , with the average of the absolute values of this difference being 0.11 wt%  $\text{H}_2\text{O}$ . In general, more scatter is seen in those amphiboles that do not satisfy our stoichiometric and charge balance constraints (the circles on Fig. A1a) as opposed to those amphiboles that do satisfy these constraints (squares on Fig. A1a). The average absolute values of the difference between calculated and measured for the former group is 0.16 wt%  $\text{H}_2\text{O}$ , whereas for the latter group the difference is 0.08 wt%  $\text{H}_2\text{O}$ . Similar results are shown on Figure A1b, as the average of the absolute values of the differences between the calculated and measured values is again 0.11 wt%  $\text{H}_2\text{O}$ . This difference is 0.07 wt%  $\text{H}_2\text{O}$  if only those samples that satisfy the stoichiometric and charge balance constraints are considered (squares), whereas this difference is 0.14 wt%  $\text{H}_2\text{O}$  for the remaining samples (circles). Relatively large differences between the calculated and measured values of  $\text{H}_2\text{O}$  in these amphiboles (Fig. 1) could result from errors in the chemical analyses, or a  $\square$  substitution mechanism not accounted for by Equations A1 and A2, or a combination of these factors.

The agreement between the calculated and observed  $\text{H}_2\text{O}$ -contents for mantle amphiboles shown in Figure A1 is sufficiently good to be useful **{AU: OK??}** for a variety of petrologic applications. This conclusion is largely independent of whether

Equation A1 or A2 is used to determine the oxy-content of the amphiboles, as both produce similar results. However, it is clear that the procedure is superior for those amphibole compositions that satisfy the constraints of both crystallographic site-occupancy and charge balance as compared to those amphiboles compositions that do not satisfy these constraints.

Table 1 lists the chemical formula of the amphibole in sample DH101E calculated from the compositional information contained in McGuire et al. in conjunction with both Equation A1 and A2. Both of these normalized formulae satisfy the cation occupancy and charge balance requirements and contain similar amounts of  $\text{H}_2\text{O}$ . The OH-content in the Z-site is 1.29 apfu when Equation A1 is used vs. 1.39 apfu when Equation A2 is used.



**APPENDIX FIGURE 1.** Comparison of the measured amount of  $\text{H}_2\text{O}$  in amphiboles vs. the amount of  $\text{H}_2\text{O}$  determined from cation-site occupancies. The solid squares represent  $\text{H}_2\text{O}$ -contents for amphiboles that satisfy stoichiometric and charge-balance constraints, whereas solid circles are amphiboles that do not satisfy those constraints. The line that represents perfect agreement between measured and predicted  $\text{H}_2\text{O}$  contents is dashed, whereas the solid line represents a linear fit to the data. The effect of analytical uncertainty on the predicted amounts of  $\text{H}_2\text{O}$  in these amphiboles is approximately equal to the size of the individual symbols. (a) The calculated amount of  $\text{H}_2\text{O}$  is based on Equation A1 (Popp et al. 1995a). (b) The calculated amount of  $\text{H}_2\text{O}$  is based on Equation A2 (King et al. 1999).