

Supplement 1 to Ridolfi et al. (2018) AMFORM, a new mass-based model for the calculation of the unit formula of amphiboles from Electron Micro-Probe analyses. American Mineralogist

Details on the procedures for sample characterization used at CNR-IGG Pavia

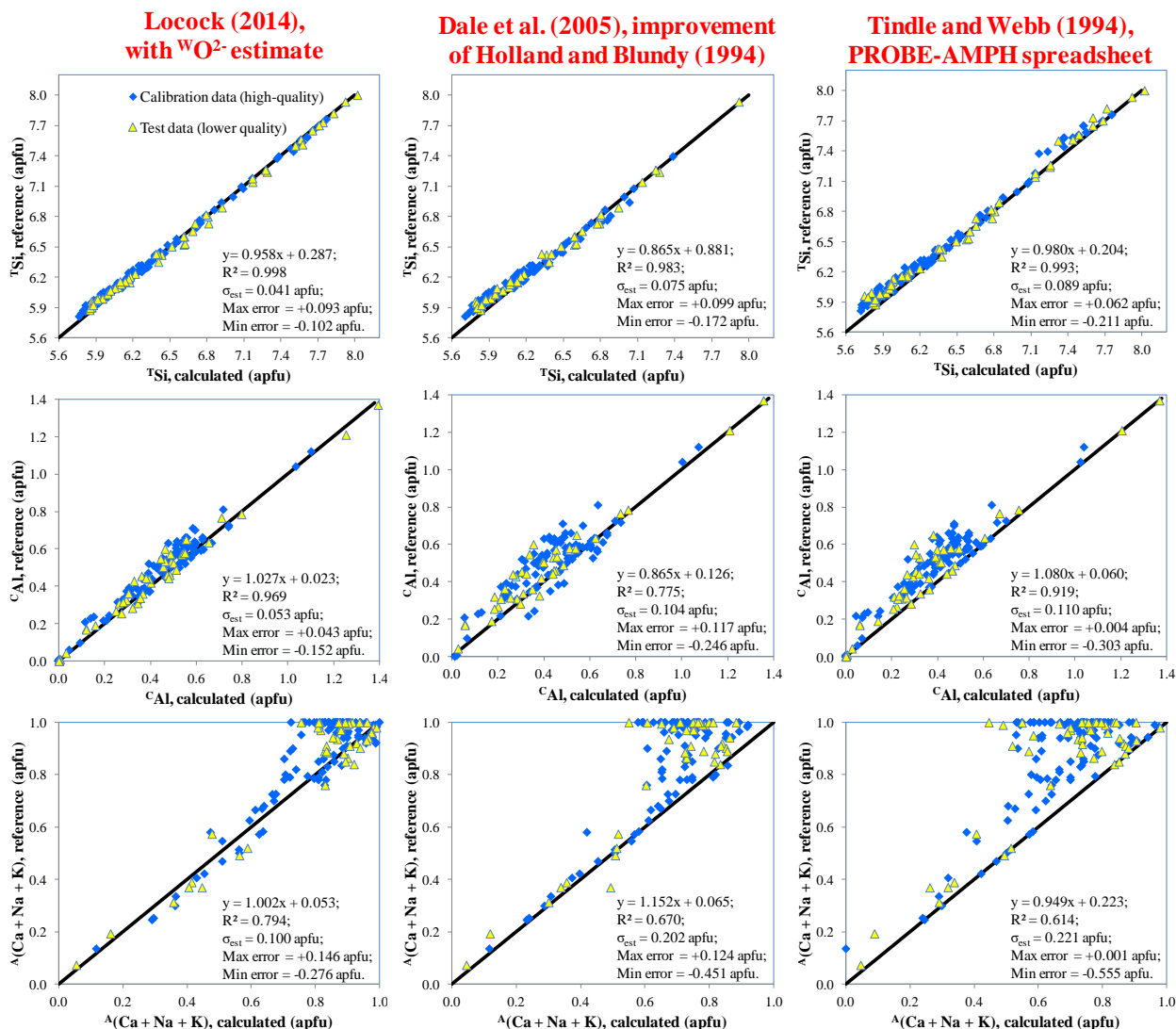
The crystals are picked up from petrological sections or from crushed material. They are chosen for crystallographic analysis on the basis of optical behavior and freedom from inclusions. Unit-cell parameter measurements and intensity data collections were performed using a Philips PW1100 diffractometer operating with MoK α radiation at 20-30 mA and 55 kV. The θ explored is 2-30°; for each dataset, two quadrants of intensity data were collected ($\pm h$, $\pm k$, $+l$) by the ω -scan mode. Accurate unit-cell dimensions are calculated by least-squares refinement of the positions of $50 \leq n \leq 60$ independent reflections with $I > 10 \sigma_I$ in the θ range 2-30°. Structure refinements are done of F using a program written in Pavia (Cannillo et al. 1983), which allows the use of neutral *versus* ionized scattering curves for all the sites where solid solution does not occur, and of combinations of ionized scattering curves in all the other sites. This procedure was proved to yield the best results in the case of complex solid-solution minerals such as the amphiboles, and is described in Hawthorne *et al.* (1995). All the refinements were done without chemical constraints, and converged to R indices of 1÷2 % for the observed reflections [$I \geq 3\sigma(I)$]. More details in Oberti et al. (2016).

Chemical analyses were mostly done (at the Department of Geological Sciences, university of Manitoba at Winnipeg) on the crystals used for structure refinement with a Cameca SX-100 electron microprobe (WDS mode, 15 kV, 20 nA, counting time 20 s, 5 μ m beam diameter). The standards used are as follows: Si and Ca: diopside (TAP); Ti: titanite (LPET); Al: andalusite (TAP); Fe: fayalite (LLiF); Mn: spessartine (LLiF); Mg: forsterite (LTAP); Zn: gahnite (LLiF); Na: albite (TAP); K: orthoclase (LPET); F: fluoro-riebeckite (TAP); Cl: tugtupite (LPET). H₂O was estimated based on 2 = (OH,F,Cl) apfu and taking into account the constraints on the group-sites based on stoichiometry and site-scattering values (for A, B and C cations) obtained from the structure refinement; the same method allowed for Fe³⁺/Fe²⁺ calculation.

H and Cl analyses were done on a Cameca 4f ion-microprobe installed at CNR-IGG (Pavia, Italy), using a 12.5 kV ¹⁶O⁻ primary beam focussed to ~ 20 μ m. Mass filtering of the primary beam allowed us to remove the OH component, which can constitute a source of H contamination. The “energy-filtering” technique was adopted to remove molecular interferences from the Cl mass spectrum and to reduce the influence of the matrix composition on the ionization of the investigated elements. A low and reproducible H background value is obtained by degassing the samples before the analysis; its fluctuation indicates that the detection limit is ~0.015% H₂O. The Si-normalised working curves for H were set up using both minerals (amphiboles, staurolites, cordierites) and glasses of basaltic composition as standards. Reproducibility of H determination is typically 3%,

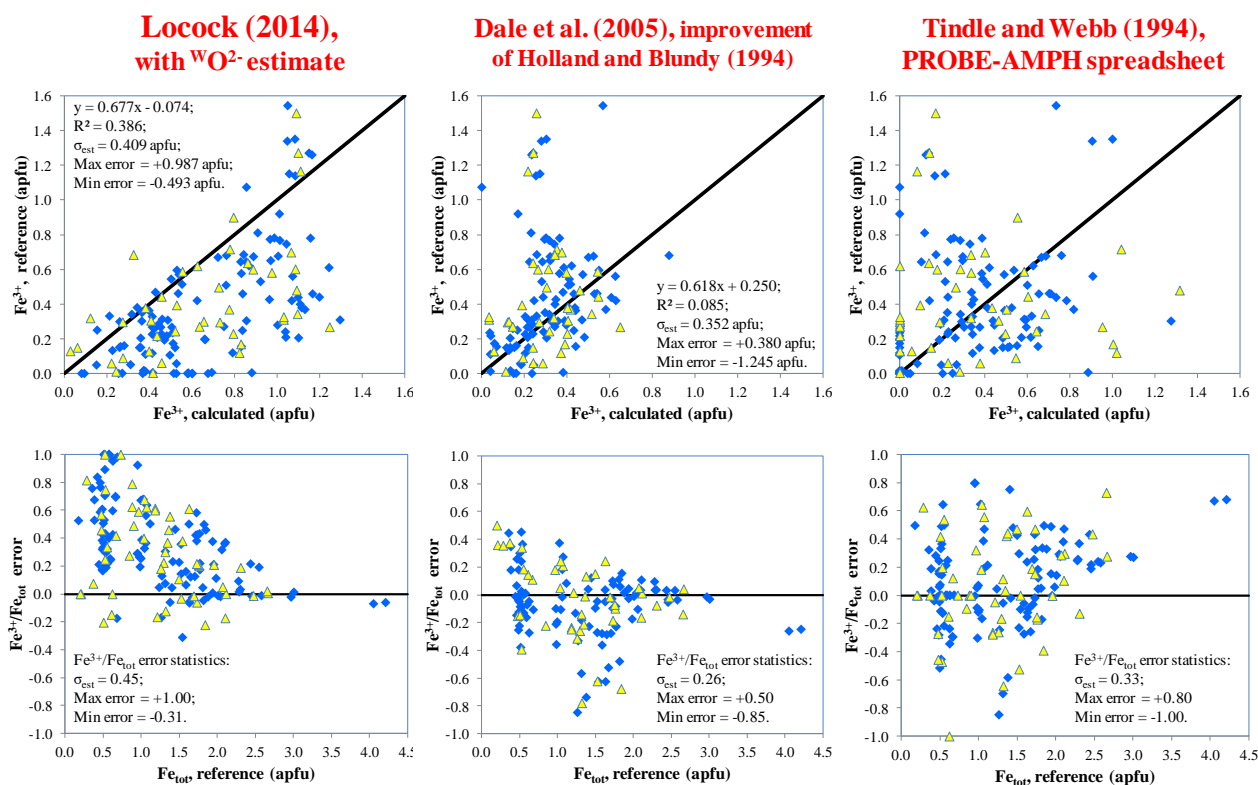
relative accuracy is 10% for $\text{H}_2\text{O} > 0.1\%$ and 30% for $\text{H}_2\text{O} \approx 0.05\%$. Further details are reported by Ottolini et al. (1995).

Additional formula testing using 114 calibration and 51 test data



Notes

- **Locock (2014):** this method tends to underestimate and overestimate $^{\text{T}}\text{Si}$ at low and high $^{\text{T}}\text{Si}$ reference contents, respectively; see Ridolfi et al. 2018 for additional comments on $^{\text{C}}\text{Al}$ and high $^{\text{A}}(\text{Ca} + \text{Na} + \text{K})$ estimations.
- **Dale et al. (2005):** this model produces large underestimations at low $^{\text{T}}\text{Si}$, low $^{\text{C}}\text{Al}$ and high $^{\text{A}}(\text{Ca} + \text{Na} + \text{K})$ reference contents (e-g); note that 28 testing data are not presented because are invalid according to Dale et al. (2005) (i.e. $f_{\text{B}} > 1$ or $f_{\text{B}} > f_{\text{A}}$); these 28 data represent Na-Ca and Na amphiboles which show negative Fe^{3+} or $^{\text{C}}\text{Al}$ contents when using the scheme of Holland and Blundy (1994) because the method is based on the IMA1997 recommendations, not accounting for the presence of $^{\text{W}}\text{O}_2$ and $^{\text{T}}\text{Ti}$.
- **Tindle and Webb (1994):** when compared to the reference cation contents, calculations performed with the PROB-AMPH spreadsheet show general $^{\text{T}}\text{Si}$, low $^{\text{C}}\text{Al}$ and high $^{\text{A}}(\text{Ca} + \text{Na} + \text{K})$ underestimations.



Notes

- **Locock (2014):** this method generally lead to Fe^{3+} and $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ overestimations which tend to increase with Fe_{tot} .
- **Dale et al. (2005):** Fe^{3+} comparison and $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ error show behaviors similar that of the AMFORM default method (Figs. 6b,c in Ridolfi et al. 2017) but a larger scattering; note, however, that most of the Na-Ca and Na amphiboles (28) testing data are not presented (invalid according to Dale et al. 2005) as they would show negative Fe^{3+} or $^{\text{C}}\text{Al}$ contents.
- **Tindle and Webb (1994):** PROB-AMPH spreadsheet does not show any relationship between calculated and reference values.

References

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