## A reassessment of the amphibole-plagioclase NaSi-CaAl exchange thermometer with applications to igneous and high-grade metamorphic rocks

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## ABSTRACT

The amphibole-plagioclase NaSi-CaAl exchange thermometer by Holland and Blundy (1994) (expression B) has been extensively applied to calcic amphibole-bearing assemblages from metamorphic and igneous rocks, whereas the more recent calibrations of the amphibole-only thermometer by Ridolfi and Renzulli (2012) (expression 2) and Putirka (2016) (expressions 5 and 6) are employed for determining amphibole-saturation temperatures in hydrous magmas. However, a test of these expressions performed on experimental data compiled from the literature reveals significant inaccuracies, tending expressions B to underestimate temperatures in high-Mg amphibole, and the amphibole-only expressions to overestimate temperatures in amphibole with either low Mg or high Al<sup>VI</sup> occupancies. Amphibole Na<sup>M4</sup> and Fe<sup>3+</sup> occupancies can also affect significantly the accuracy of expression B.

In this work, we present three new accurate calibrations (expressions A1, A2, and B2) of the amphibole-plagioclase NaSi-CaAl exchange thermometer calculated by robust regression methods based on multiple maximum-likelihood estimators (MM-estimators; Yohai 1987), considering various calibration and test data subsets to evaluate the robustness of the derived parameters in the thermodynamic models, and the accuracy and precision of the expressions. Non-ideality in plagioclase was corrected using the ternary feldspar solution model of Elkins and Grove (1990) in expressions A1 and A2, whereas the simplified version of the Darken's Quadratic Formalism (DQF) approach of Holland and Powell (1992) was used in expression B2. The formulation of the multisite macroscopic solution model of Powell and Holland (1993) was used for deriving the mixing parameters of amphibole in the three calibrations. Expression B2 is strictly pressure-independent, while the two others show a negligible dependence on pressure for plagioclase with low orthoclase component (<11 mol%). The three calibrations yield an overall precision close to those reported for the tested amphibole-based thermometers but are significantly more accurate, a requisite for an unambiguous interpretation of precision.

The new expressions can be used in a wide range of igneous and high-grade metamorphic rocks that bear subcalcic to calcic amphibole and oligoclase or more calcic plagioclase. However, they must be applied only to amphibole-plagioclase pairs whose compositions lie in the optimal region of use prescribed in the work.

Keywords: Thermometry, calcic amphibole, plagioclase, mixing properties, high-grade metamorphic rocks, metaluminous igneous rocks