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Barometers behaving badly: Assessing analytical and experimental error on clinopyroxene thermobarometry

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The composition of clinopyroxene (Cpx) and co-existing Cpx-liquid pairs are frequently used to calculate crystallization/re-equilibration pressures in igneous systems to determine pre-eruptive magma storage and staging conditions. Canonical uncertainties are often assigned to calculated pressures based on reported fits to the calibration dataset, yet the errors on Cpx-based barometers have not been rigorously assessed. We find that large variations in Cpx compositions from a single experiment for elements with low concentrations (<1 wt%, e.g., Na_2O, MnO) largely result from analytical imprecision relating to counting statistics (5-50%). In contrast, the observed variation in major elements (Al_2O_3, SiO_2, TiO_2) greatly exceeds that expected from counting statistics, indicating that disequilibrium processes (e.g., sector zoning) may be common in experimental products. Using Monte-Carlo approaches to simulate major element variation, we demonstrate that analytical imprecision alone can generate pressures spanning ~4 kbar of uncertainty for Cpx-only barometers, and ~6 kbar for Cpx-Liq barometers. This results from the high imprecision of Na_2O measurements (~10-40%), producing a large error in the pressure-sensitive Jadeite component. 43% of experimental charges used to calibrate existing barometers report ≤5 Cpx analyses per experiment. Thus, analytical imprecision, in addition to variability in Cpx compositions resulting from disequilibrium processes, has not been adequately averaged out.

This noise causes all Cpx-based barometers to exhibit large errors (±3 kbar) when applied to global calibration datasets. The spread of pressures resulting from analytical imprecision should also be considered when applying Cpx-based barometers to natural systems before attributing a spread of calculated pressures to transcrustal magma storage. We suggest various tweaks to analytical and experimental protocols to improve experimental datasets used to calibrate Cpx-based barometers, such as increased count times and/or beam currents for low concentration elements, increasing number of analyses per experimental charge, resolving interlaboratory analytical offsets and improved data reporting. Following these protocols as a community will produce a more precise dataset to calibrate the next generation of precise, Cpx-based barometers. Acquiring new, higher quality experimental data will likely be more fruitful than applying big data approaches (e.g. Machine Learning) to existing, lower quality experimental datasets.