ASSESSING THE ACCURACY OF CLINOPYROXENE THERMOBAROMETERS IN THE MARTIAN NAKHLITE SYSTEM.

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Introduction: The nakhlites are clinopyroxene-rich cumulate rocks that were emplaced on the Martian surface ~1.3 billion years ago (e.g., [1]). Based on chemical zoning, the phenocryst cores of nakhlites are thought to have formed in the deep crust, while the rims crystallized on the surface [2]. This suggests that the pressure and temperature (P-T) conditions of the nakhlite deep crustal chamber might be constrained by studying the minerals in the rocks, potentially offering new insights into Martian crustal evolution [3].

However, accurately estimating the formation P-T conditions of Martian nakhlite meteorites presents several challenges: (1) the cumulate texture of these rocks complicates the determination of the equilibrium parental magma compositions (e.g., [4]); (2) the mineral assemblages are simple, with clinopyroxene being the dominant phenocryst and lesser amounts of olivine and plagioclase (e.g., [5]); (3) there is a significant lack of P-T-controlled crystallization experiments under Martian conditions, with only one study [6] providing atmospheric crystallization data for nakhlites. These challenges mean that clinopyroxene-only thermobarometers remain almost the only method for quantifying the crystallization P-T conditions of nakhlites.

To date, the Ti/Al ratio in pyroxenes from Martian rocks has been linked to formation pressure [7]. Using parental magma compositions from shergottites, [8] calibrated this correlation at pressures above 10 kbar, yielding consistent results. As a result, the pyroxene Ti/Al ratios have been widely adopted as a reliable barometer for Martian basalts (e.g., [9–10]). However, it is important to note that this barometer has not been calibrated for low pressures or for the nakhlite system, and thus remains largely qualitative. Recently, several clinopyroxene thermobarometers have been developed using empirical formula fitting or supervised machine learning techniques. However, these methods have primarily been tailored to terrestrial conditions and have not been tested under Martian conditions.

Here we evaluate the performance of seven commonly used clinopyroxene-only thermobarometers [11–17] for estimating P-T conditions in the Martian nakhlite system. To do so, we use the atmospheric crystallization experimental results for nakhlites reported in Tables 1–2 of [6]. Our focus is on assessing the performance of these thermobarometers at low pressures, as the Martian crust, with a pressure range of 0–4.5 kbar (for a 50 km thick crust), falls within the 2σ error range of most existing thermobarometers.

Results and Discussion: We divided the experimental results into two groups: one representing the clinopyroxene rims (n=6), characterized by higher TiO_2 (>0.8 wt%) and Al_2O_3 (>3 wt%) contents, similar to the rims of clinopyroxene in nakhlites, and the other representing the clinopyroxene cores (n=6), with lower TiO_2 (<0.6 wt%) and Al_2O_3 (<1.7 wt%) contents, similar to the cores of clinopyroxene in nakhlites. All experiments were performed at atmospheric pressure (0.001 kbar).

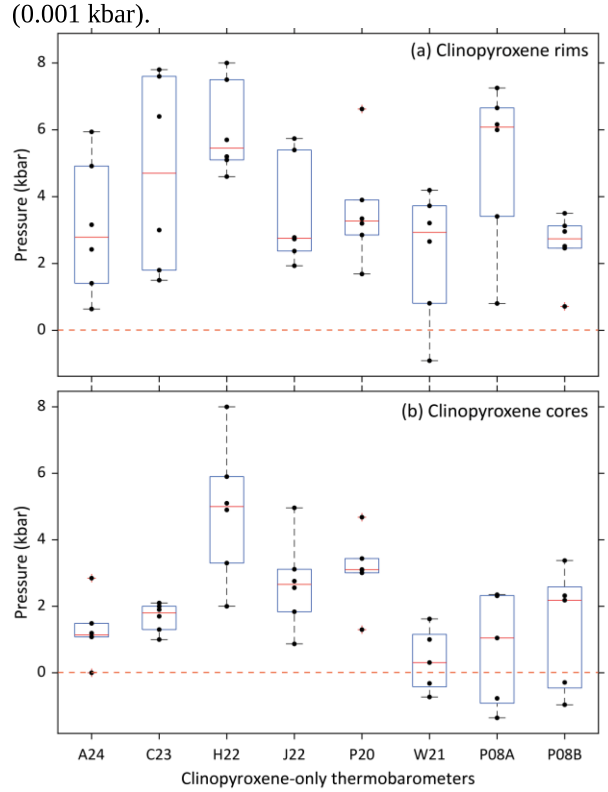

Figure 1. Comparative bar charts showing predicted pressure values from barometers (bars) versus experimental values (red dashed horizontal line). Thermobarometer abbreviations: A24 [11]; C23 [12]; H22 [13]; J22 [14]; P20 [15]; W21 [16]; P08A – Eqn. 32a & 32d in [17]; P08B – Eqn. 32b & 32d in [17].

We applied eight clinopyroxene-only thermobarometers to estimate the P-T conditions of the experimental data. Five of these thermobarometers (A24, C23, H22, G22, P20) were calibrated using machine-learning techniques, while three (W21, P08A, P08B) were based on empirical formula fitting. The results of our evaluation are shown in Figures 1 (pressure) and 2 (temperature).

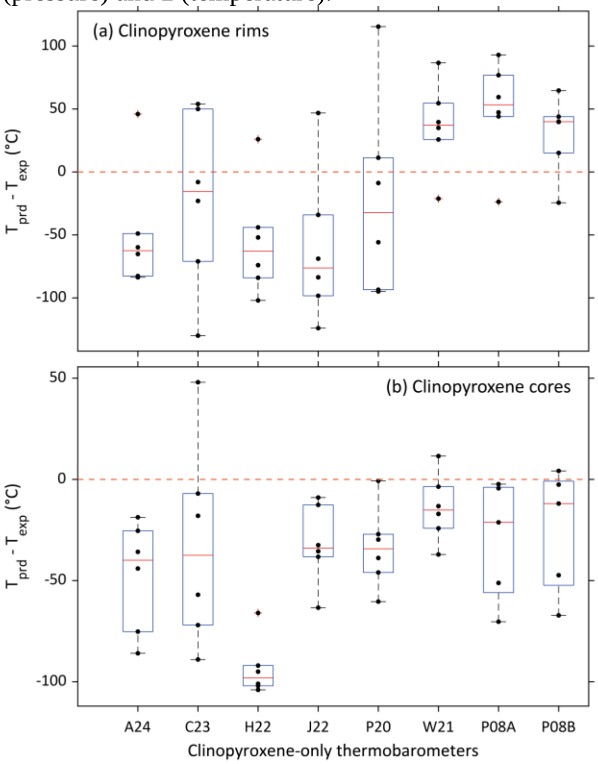

Figure 2. Comparative bar charts showing predicted temperature values from thermometers (bars) versus experimental values (red dashed horizontal line). Thermobarometer abbreviations are the same as in Figure 1.

Pressure estimates. All barometers estimated formation pressures for the nakhlite clinopyroxene rims that were anomalously higher than both the experimental values (~3–6 kbar) and the formation pressures of cores (~1–5 kbar). This discrepancy is mainly due to the high TiO_2 and Al_2O_3 contents in the rims, which result from disequilibrium crystallization under fast kinetics. Therefore, clinopyroxene-only barometers cannot reliably estimate the formation pressures of nakhlite clinopyroxene rims.

All machine-learning-based barometers predicted the formation pressures of the nakhlite clinopyroxene cores to be higher than the actual values by ~1–5 kbar, with notably large 1σ standard deviations ranging from 0.4 kbar to 1.9 kbar. In contrast, the empirical formula-based barometers produced pressure estimates closer to the actual values, but still exhibited large 1σ standard deviations (ranging from 0.9 kbar to 1.7 kbar). Among these, the barometer proposed by [16] provided the most accurate estimate for the formation pressure of nakhlite clinopyroxene cores, with an average overestimation of +0.4 kbar and a 1σ precision of 0.9 kbar.

Temperature estimates. The machine-learning-based thermometers underestimated the rim formation temperatures by 20–80 °C, while the empirical formula-based thermometers overestimated the rim formation temperatures by 30–50 °C. Considering both accuracy and precision, we recommend using [11] and [16] to estimate the lower and upper limits of the rim formation temperatures, respectively.

For the clinopyroxene cores, all thermometers systematically underestimated the temperatures by 20–100 °C. The thermometer proposed by [16] provided the best estimates, with an average underestimation of 14 °C and a 1σ precision of 15 °C.

Conclusions: We recommend using the clinopyroxene-only barometer proposed by [16] to estimate the formation pressures of nakhlite clinopyroxene cores, which shows an average overestimation of +0.4 kbar. For estimating the formation temperatures of nakhlite clinopyroxene rims, we recommend using the thermometer proposed by [11] and [16], with an average estimation error of -68°C/ +48°C. Finally, the thermometer proposed by [16] provides the best estimate for the formation temperatures of nakhlite clinopyroxene cores, with an average estimation error of -14 °C.

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