

APPENDIX. PROPAGATION OF ANALYTICAL ERRORS IN SINGLE-CLINOPYROXENE GEOBAROMETRY

The Cr-in-Cpx barometer (Nimis and Taylor, 2000) is expressed as

$$P(\text{kbar}) = -\frac{T(\text{K})}{126.9} \cdot \ln a_{\text{Cr}} + 15.483 \cdot \ln\left(\frac{\text{Cr}\#}{T(\text{K})}\right) + \frac{T(\text{K})}{71.38} + 107.8 \quad (1)$$

where $a_{\text{Cr}} = \text{Cr} - 0.81 \cdot \text{Na} \cdot \text{Cr}\#$ and $\text{Cr}\# = \text{Cr}/(\text{Cr}+\text{Al})$, with elements in apfu. Although the effect of K on Cpx barometry was unknown, Nimis and Taylor (2000) suggested that any K should be added to Na in P calculations. Assuming random error sources, the uncertainties on pressure estimates can be expressed with a normal error propagation function, i.e.,

$$\sigma P = \sqrt{\left(\frac{\partial P}{\partial \text{Cr}} \cdot \sigma_{\text{Cr}}\right)^2 + \left(\frac{\partial P}{\partial \text{Al}} \cdot \sigma_{\text{Al}}\right)^2 + \left(\frac{\partial P}{\partial \text{Na}} \cdot \sigma_{\text{Na}}\right)^2 + \left(\frac{\partial P}{\partial T} \cdot \sigma T\right)^2} \quad (2)$$

Calculation of σP requires knowledge of analytical uncertainties on Cr, Al, Na and T . The influence of analytical uncertainties on the very minor K contents can safely be neglected. Uncertainties on T estimates can be derived from reproducibility of temperatures of experiments in two-pyroxene-bearing assemblages using the enstatite-in-Cpx thermometer (± 30 – 40°C ; Nimis and Taylor 2000). Accurate evaluation of EMP uncertainties is not straightforward, because analytical errors primarily depend on both the absolute element concentrations and on the analytical conditions adopted for the analysis.

In this appendix, we will investigate the effect of EMP uncertainties on pressure estimates for compositionally diverse clinopyroxenes. As a first step, we will evaluate the analytical errors for different analytical conditions and for a specific set of clinopyroxene compositions through repeat EMP measurements on compositionally homogeneous areas of selected cpx grains, and evaluate the propagated uncertainties on P estimates by calculating P for each analysis. We then apply the error propagation function (Equation 2) to a great variety of natural clinopyroxene compositions, assuming model analytical uncertainties derived from the first test.

First step: evaluation of uncertainties vs. analytical conditions

We selected seven clinopyroxenes having a_{Cr} between 0.0016 and 0.0188 apfu, characterized by various proportions of Al, Cr and Na, and equilibrated in a wide range of P – T conditions (Appendix Table 1). Appropriate compositions were found in four clinopyroxene xenocrysts from the Novinka kimberlite (this study) and three clinopyroxenes from three well-studied garnet peridotites. Description of the garnet peridotite samples is reported in Supplementary Material 3.

Chemical analyses were carried out with a CAMECA SX-50 electron microprobe (IGG–CNR, Padua, Italy), equipped with four wavelength-dispersive spectrometers using one LIF, one PET, and two TAP crystals. Natural and synthetic minerals (diopside for Ca and Si, albite for Na, orthoclase for K, and pure Al, Mg, Cr, Fe, and Mn-Ti oxides) were used as standards. X-ray counts were converted into weight percent oxides by using the CAMECA-PAP program. Each clinopyroxene grain/portion was first analyzed for all elements adopting routine analytical condition, i.e., 1 μm electron beam, 20 kV accelerating voltage, 15 nA beam current, and a counting time of 10 s for peak and 10 s for background (i.e., 5 s on each side of the peak). The most mobile elements were always analyzed first in order to minimize their migration under the electron beam. The sequence of element analyses on each spectrometer was thus as follows: Fe, Mn, Cr (LIF); Si, Al (TAP); Na, Mg (TAP); K, Ca, Ti (PET). This preliminary investigation allowed us to select compositionally homogeneous areas and provided us with average compositions to be used for calculation of matrix effects in subsequent analytical sessions and for preliminary thermobarometry (Appendix Table 1).

The same clinopyroxenes were then analyzed again for Al, Cr and Na using increasing beam currents and counting times (Appendix Table 2). Five analytical sessions were carried out, during which 15 individual point analyses were acquired on the same, homogeneous areas of each clinopyroxene. The analyses were carried out on a grid of 3 x 5 analytical spots (maximum side 20

μm). To limit element migration under the electron beam, before each session the grid was translated by 3–4 μm , within the previously defined homogeneous areas. Calcium was also measured on the same spots as a further check for compositional homogeneity. The four elements were analyzed simultaneously with the four independent spectrometers. Observed absolute variations in CaO weight percentages between individual point analyses were always ≤ 0.5 wt%. No systematic variations in X-ray counts for Na were observed using different beam currents (i.e., 15 nA and 40 nA), not even after a 300-s count period, implying that Na did not significantly mobilize under the electron beam during our analyses (cf. Nielsen and Sigurdsson 1981). No analyses for which any measured concentration departed by more than 3 standard deviations from the mean were obtained. The average compositions obtained during the five test sessions on each selected clinopyroxene are reported in Appendix Table 3.

For each point analysis, $Cr\#$, a_{Cr} and Cr-in-Cpx pressure were calculated. Pressures were calculated using fixed input temperature values, which were obtained by applying the enstatite-in-Cpx thermometer, at P given by the Cr-in-Cpx barometer, on the compositions derived from the preliminary analyses of the samples (Appendix Table 1). Statistical parameters (mean values, standard deviations, and quantiles) for all relevant variables are reported in Appendix Table 3 and illustrated in Appendix Figure 1.

The relative uncertainties on the measured Al, Cr and Na concentrations decrease smoothly with increasing beam current, counting times, and element abundances (Appendix Table 3). This allowed us to model analytical uncertainties as functions of clinopyroxene composition for each set of analytical conditions (Appendix Table 4). The standard deviations on P estimates drastically change with changing analytical conditions (σ as high as 1.1 GPa using the lowest beam current and counting times) and clinopyroxene composition (Appendix Table 3 and Fig. 1).

The relationships between P uncertainties and composition can be explained considering the topology of the Cr-in-Cpx barometer expression (Equation 1). In equation (1), P is related to a_{Cr} and

$Cr\#$ through two logarithmic functions. This enhances error propagation with decreasing a_{Cr} and $Cr\#$. Owing to its greater weight in the equation, the effect of the a_{Cr} logarithmic term tends to be dominant in terms of error propagation. This accounts well for the larger P uncertainties obtained for the clinopyroxene Nov-42 ($a_{Cr} = 0.0016$ apfu) with respect to clinopyroxene Uv61/91 ($a_{Cr} = 0.0081$ apfu), in spite of their similar a_{Cr} uncertainties (Appendix Table 3). It also explains the progressively larger, non-systematic deviations from orthopyroxene–garnet pressures at lower a_{Cr} (Figs. 2 and 4). Moreover, because of the logarithmic relation, the distribution of propagated errors due to a_{Cr} uncertainties tends to be skewed towards the positive side.

Whereas the effect of the $Cr\#$ logarithmic term on error propagation is marginal, $Cr\#$ has a major effect on the uncertainties of the a_{Cr} parameter. In particular, a higher $Cr\#$ will enhance propagation of Na uncertainties on a_{Cr} and, therefore, on P . This explains the lower P uncertainties (and their less pronounced variations between different analytical sessions) obtained for clinopyroxene Nov-80, which is characterized by low a_{Cr} (0.003 apfu) and low $Cr\#$ (0.13), compared with those obtained for compositions with higher $Cr\#$ values (Appendix Table 3 and Fig. 1).

Second step: P uncertainties in the natural clinopyroxene compositional space and optimum analytical conditions for clinopyroxene barometry

The above test showed that the effect of analytical errors on the precision and accuracy of the calculated pressure strongly increases with decreasing a_{Cr} and with increasing $Cr\#$. For any clinopyroxene composition, minimum analytical conditions should be defined for which analytical errors propagate acceptable errors on pressure estimates. For this purpose, a more extended test on a comprehensive set of clinopyroxene compositions is needed. We have used the database of well-equilibrated xenoliths of Nimis and Grütter (2010) as our test material. Temperatures for each xenolith were calculated using the thermometer of Taylor (1998) at P given by the orthopyroxene–garnet

barometer of Nickel and Green (1985; with modifications by Carswell 1991, his equations E6 and E9, assuming no ferric iron). The T uncertainty was fixed at 40 °C (cf. Nimis and Taylor 2000). Uncertainties on clinopyroxene Cr, Al and Na analyses were calculated for each xenolith for five combinations of analytical conditions, taking into account the results of our previous analytical test (Appendix Table 4). Uncertainties on Cr-in-Cpx pressures were then calculated by normal error propagation of the five resulting sets of analytical uncertainties (Equation 2).

As expected, the calculated uncertainties increase with decreasing a_{Cr} and increasing $Cr\#$ values (Fig. 3), reaching 1.8 GPa when a_{Cr} is <0.002 apfu and the lowest current and counting times are assumed. These results can be used to determine an approximate compositional threshold below which pressure estimates become too sensitive to analytical errors. We consider a propagated uncertainty of ± 0.25 GPa on the calculated P , including the effect of both analytical and thermometric errors, to be a reasonable limit. Taking into account the standard error of estimate of the barometer calibration (± 0.23 GPa), this limit should ensure an overall uncertainty smaller than ± 0.4 GPa. We found that simplified thresholds based on the $a_{Cr}/Cr\#$ ratio (Appendix Table 2) permit discrimination of compositions for which P uncertainties are acceptable to within a 95% confidence limit.