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Iron valence systematics in clinopyroxenes from oceanic basalts: re-evaluating stoichiometric estimates of clinopyroxene ferric iron contents

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Clinopyroxene is a major constituent of most upper mantle and crustal rocks across all tectonic settings. The general formula for clinopyroxene is $M2M1T_2O_6$, where M2 is a distorted octahedral site, M1 is a regular octahedral site and T is a tetrahedral site, allowing it to incorporate diverse major cations. This makes it particularly valuable for estimating the thermochemical conditions under which magmas form and crystallise, as well as the timescales over which these processes occur. However, the abundance of ferric iron (Fe^{3+}) in magmatic clinopyroxenes and the substitution mechanisms by which it is incorporated remain highly uncertain, including in the oceanic basalts that dominate global magma fluxes. The few direct determinations of Fe valence by Mössbauer spectroscopy that do exist suggest that ratios of Fe^{3+} to total Fe (i.e., $Fe^{3+}/\Sigma Fe$) are well above zero in many clinopyroxenes and can reach up to 0.6 in mafic alkaline rocks, implying Fe^{3+} is a major but cryptic constituent of clinopyroxene in many systems. To address these uncertainties we performed Mössbauer spectroscopy and high-precision electron probe microanalysis (EPMA) on end-member and single crystal clinopyroxenes to critically re-evaluate the potential for determining clinopyroxene $Fe^{3+}/\Sigma Fe$ by stoichiometry, an accessible but discredited approach of determining $Fe^{3+}/\Sigma Fe$. We find that stoichiometric determinations following Droop (1987) reproduce Mössbauer results within uncertainty ($1\sigma \sim 0.03$). We then performed high-precision EPMA on clinopyroxenes in oceanic basalts from Iceland and the Azores that range from tholeiitic basalts to tephrites to generate an internally consistent dataset clinopyroxene compositions and $Fe^{3+}/\Sigma Fe$ systematics. Clinopyroxene $Fe^{3+}/\Sigma Fe$ ranges from 0 to 0.3 in tholeiitic basalts but extends up to 0.5 in tephrites. Our results suggest that most Fe^{3+} is incorporated as esseneite ($CaFe^{3+}AlSiO_6$) rather than aegirine ($NaFe^{3+}Si_2O_6$). Finally, we explored whether current models of Fe^{3+} partitioning could be used to determine magmatic oxygen fugacities. Our initial explorations based on stoichiometric calculations suggest that Icelandic tholeiites evolve close to FMQ+1 while Azorean basalts evolve nearer to FMQ+2, which is not inconsistent with literature data. They also highlight that more experiments are needed to develop robust clinopyroxene oxybarometers applicable at crustal conditions.

Droop (1987). Min Mag 51, 431–435.