



Electrochemical effects of magmatic crystallisation: cyclic units of the Bushveld Igneous Complex

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The Upper Critical Zone (UCZ) of the Bushveld Igneous Complex displays spectacular layering in the form of cyclic units comprising a basal chromitite layer overlain by a sequence of silicate cumulates in the order, from the bottom to the top, pyroxenite-norite-anorthosite. Electron microprobe and laser ablation ICP-MS analyses of chromite and silicate cumulate minerals in the cyclic units between the UG2 chromitite and the Merensky reef revealed variations in major and trace element compositions that are difficult to reconcile with existing models of cumulate mineral-melt evolution. The anomalies in mineral chemistry are best developed at sharp contacts of chromitites with adjacent anorthosite and pyroxenitic cumulates. At the contacts, major element characteristics of chromite composition change abruptly from high and stable $\text{Mg}/(\text{Mg}+\text{Fe}^{2+})$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$ typical for cumulus chromitites to variable and generally low values in chromite crystals disseminated in silicate cumulates. Chromites from different types of cumulates also differ in Sc, V, Ni and Zn contents. The abrupt changes in chromite composition mark the contacts regardless of the thickness of the chromitite layer and estimated mass proportions of chromite to intercumulus liquid. Chemical variations, which defy a simple explanation, are also observed in plagioclase. In addition to previously revealed inconsistency between chemical trends of cumulus plagioclase and orthopyroxene in the UCZ cyclic units our study demonstrates that intercumulus, poikilitic plagioclase cementing chromitite layers has anomalously low Li, K, Rb concentrations and K/La values.

Summarising previous studies and the new trace element data we propose a model of post-cumulus re-crystallisation leading to consolidation of a modally layered crystal-liquid mush into a sequence of nearly monomineral layers of chromitites, pyroxenites and anorthosites, which defines the cyclic units. The crucial element of the model is the establishment of redox potential gradients at contacts between chromite-rich cumulates and adjacent layers dominated by silicate minerals (plagioclase, olivine, orthopyroxene) due to peritectic reactions between the crystals and intercumulus liquid. Because basaltic melts are ionic electrolytes with Na^+ as the main charge carrier, a redox potential gradient in such conductive media should induce electrochemical migration of Na^+ and other alkali ions. Preliminary estimations based on the observed variations in ferric/ferrous iron ratios in chromite from the Bushveld cyclic units show that the redox gradient and the resulting electrochemical flux of Na^+ ions would be sufficient to mobilize about one-third of the total Na content of a metre-thick mush layer within 10 years. Electrochemical migration of Na is expected to cause re-melting of previously formed cumulates and major changes in modal mineral proportions, which eventually may lead to the formation of sharply divided monomineral layers. The processes is enhanced by the presence of cumulus chromite but, in principle, it may operate in any type of cumulates where ferrous and ferric iron species are contrastingly distributed between crystalline and liquid phases..