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# Phase equilibrium constraints on the production and storage of peralkaline silicic magmas: insights from Kenya and Pantelleria

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The origin of peralkaline silicic rocks is still obscure and stands perhaps as one of the last major unsettled issues in classic igneous petrology. The debate goes back to the end of the 18<sup>th</sup> century and despite intensive petrological, geochemical and laboratory efforts the consensus has yet to emerge as to which mechanisms produce peralkaline derivatives. Bowen (1937) first proposed that the shift from metaluminous to peralkaline field was due to extensive fractionation of calcic plagioclase. Perhaps the best illustration of such an hypothesis is provided by the Boina rock series in the Ethiopian rift studied by Barberi et al. (1975). However, such an hypothesis still awaits experimental confirmation. A different view has been expressed for the origin of peralkaline rhyolites erupted in the central part of the Kenya Rift Valley. There, a partial melting of crustal protoliths has been advocated on the basis of geochemical arguments (Macdonald et al., 1987). The origin of peralkaline rocks at Pantelleria, the type locality of peralkaline rhyolites, is also a matter of debate. Mahood et al (1990) have proposed an origin via partial melting of Fe-rich differentiates of transitional basalts, whilst Civetta et al. (1998) have argued that pantellerites could be produced via extensive fractionation of their putative parent basalts. The diversity of opinions reflects in part that, presumably, there is not only one mechanism at work. But it is also due to the fact that most experimental studies devoted to the clarification of this problem have failed in producing decisive arguments during more than one century of intense debate.

We have addressed this problem by performing phase equilibrium experiments on representative rock types from two key localities: one in Kenya, the Olkaria volcanic field near Naivasha lake, and one in Italy, at Pantelleria island.

We first consider the origin of Kenyan rocks. Experiments were conducted on three representative comendites (Olkaria proper) and one pantellerite (Eburru). Conventional phase equilibrium experiments were performed on powders of natural dry aphyric obsidians under a wide range of P-T-H<sub>2</sub>O-fO<sub>2</sub> conditions. Experiments reveal that liquidus temperatures are progressively depressed as peralkalinity increases, irrespective of T-P-H<sub>2</sub>O and fO<sub>2</sub> conditions applied: a pantellerite rhyolite has lower crystallisation temperatures than comendites *sensu lato* despite it being iron richer and silica poorer. The main fractionating phases are quartz and alkali feldspar in the ratio of 1/2, respectively, and this cotectic proportion is maintained over most of the crystallisation interval. Ferromagnesian minerals include sodic-calcic clinopyroxenes and amphiboles, in addition to biotite, fayalite and scarce oxides, mostly ilmenite. The fO<sub>2</sub> exerts a dramatic control on ferromagnesian phase stabilities. High fO<sub>2</sub> promotes sodic clinopyroxene, while low fO<sub>2</sub> favours fayalite, biotite and sodic amphibole, in addition to ilmenite. Calcic clinopyroxene (hedenbergite) breaks down to a fayalite-fluorite assemblage at very low fO<sub>2</sub>, below NNO-1. In contrast, large variations in fO<sub>2</sub> appear to exert little effect, if any, on the crystallisation curves of tectosilicates.

The chemical trends displayed by the residual liquids illustrate the control of the solid fractionating assemblage. Conditions in which the crystallising feldspar is less peralkaline than the coexisting liquid, promote the peralkaline character of the derivative liquids, exemplifying the orthoclase effect put forward by Bailey and Schairer (1964). Under those conditions, as soon as the derivative liquids reach an alkali index higher than 1.10, further alkali feldspar fractionation produces strongly peralkaline liquids. Such a process is halted or damped whenever a strongly sodic bearing phase crystallises: at high  $fO_2$  sodic pyroxene (acmite) plays that role, whilst at low  $fO_2$ , sodic amphiboles (arfevdsonite or riebeckite) inhibit strong peralkaline enrichment. The overall process is capable of producing pantellerite-like liquids starting from almost metaluminous rhyolites having alkali indices of 1.05. Fractionation of bulk pantellerite magma compositions (Eburru-type) yields even more extreme rhyolite compositions having 12-13 wt% FeO, at temperatures as low as 700°C. The critical factor that allows bifurcation of liquid compositions from the crystallisation of a near metaluminous rhyolite towards the peralkaline field appears to be the presence of calcic pyroxene, whose stability is controlled by  $fO_2$ . Our results show that as long as Ca-px is stable, a marginally peralkaline rhyolite has little potential to increase the alkali index of its derivatives. In contrast, when  $fO_2$  drops below NNO-1, the breakdown of Ca-px produces derivative liquids which are slightly more peralkaline than coexisting feldspar. Then, the subsequent massive crystallisation of feldspar leads to a runaway increase of liquid sodium content (and Fe). Our experiments show that strongly peralkaline liquids can be produced from a near metaluminous rhyolitic source under appropriate  $fO_2$  conditions, and therefore point to an origin of some peralkaline series controlled by intensive parameters ( $fO_2$ ) rather than solely by source composition. The production of Kenyan peralkaline rhyolites does not necessitate neither a basalt nor a trachyte parent magma as commonly envisaged. Application of experimental results to rocks show that pre-eruption conditions of Olkaria magmas were characterised by temperatures below 750°C, water-rich conditions (ca 5 wt % H<sub>2</sub>O in melt) and  $fO_2$  around FMQ. This illustrates that water-rich magma can be reduced as well.

We now consider Pantelleria rocks. Here we have been working on a basalt and a rhyolite end-members, both representative of the bimodal association that typifies most alkaline magma series. Pantellerite from Pantelleria displays higher crystallisation temperatures than that from Eburru in Kenya, yet liquidus temperatures under water-poor conditions do not greatly exceed 850°C. In addition, it crystallises only alkali feldspar in the temperature range 750-800°C, whilst that from Eburru co-crystallise both quartz and feldspar. Aenigmatite crystallises only at low H<sub>2</sub>O at these temperatures, while it is absent in Eburru. These differences in phase relationships reflect small but perceptible changes in bulk rock composition and show that the pantellerite phase relationships need to be worked out on a case by case basis if aimed at constraining storage conditions. Work on basalt has been performed in the pressure range 0.5-3 kb, temperatures between 900 and 1050°C,  $fO_2$  between NNO-2 up to NNO+1 and various melt H<sub>2</sub>O contents. The crystallising phase assemblage is dominated by calcic clinopyroxene, olivine, plagioclase, FeTi oxides and calcic amphibole, the latter only at pressures above 1 kb. Both Cpx and Ol are liquidus phases under H<sub>2</sub>O rich conditions, being joined by Pl at low H<sub>2</sub>O content. The experiments broadly reproduce mineral compositions and proportions observed in natural Pantelleria basalts. They suggest that moderately reducing conditions are required to match oxide occurrence, with  $fO_2$  around NNO.

Liquid composition trends show the following features. When compared to dry experiments performed by Mahood and Baker (1986) on Pantelleria basalts, the role of water is clearly one of favouring differentiation towards oversaturated derivatives. The crystallisation of Pantelleria basalts under dry conditions changes little the SiO<sub>2</sub> content of

residual liquids, at either 8 kb or 1 bar, while introduction of water allows a smooth but continuous increase in SiO<sub>2</sub> content during crystallisation. As a result, dry fractionation of basalt is unable to produce intermediate magma compositions that would fill the chemical gap (Daly gap) documented in many alkaline provinces, including at Pantelleria. In contrast, fractionation of a water-bearing basalt yields derivatives that progressively fill such a gap and clearly trend toward the felsic end-member (ie the pantelleritic rhyolites). However, the most SiO<sub>2</sub>-rich liquid so far produced in our experiments are andesitic (57 wt% SiO<sub>2</sub>) in composition after 78 wt% fractionation, and are still metaluminous.

Because basalt charges containing less liquid are not suited for probe analyses, we have reproduced a synthetic mix of the most fractionated liquid obtained by basalt crystallisation (57 wt% SiO<sub>2</sub>, 16.7 wt% Al<sub>2</sub>O<sub>3</sub>, 8.7 FeO, 5.8 wt% CaO, at 1000°C, 500 bar) and carried out several phase equilibrium experiments on this synthetic mix in an effort to extend the liquid line of descent toward more silicic derivatives. Experiments were done at 500 bar and 950 and 900°C at around NNO and with various H<sub>2</sub>O. The experiments thus reproduce a fractionation stage between early formed crystals and residual liquid. The liquid compositions generated this way become, as expected, more silicic, reaching trachyte-rhyodacitic compositions after 50 wt% further crystallisation, that nearly touch the most mafic term of the Pantelleria felsic array in a Harker-type projection. In detail however, the experimental liquids display several compositional mismatches relative to their natural counterparts. First of all they are still metaluminous, being too rich in Al<sub>2</sub>O<sub>3</sub> showing clearly that the peralkaline divide line has not been crossed in our experiments. They are also too rich in K<sub>2</sub>O (up to 6 wt%), while natural pantellerites have K<sub>2</sub>O content in the range 4-5 wt%. A close inspection shows that the Al<sub>2</sub>O<sub>3</sub>/CaO balance of the residual liquid is controlled by the relative proportion of plagioclase and clinopyroxene, which is itself controlled by melt H<sub>2</sub>O content and pressure, at fixed temperature. Experiments performed at 500 bar yield a too high cpx/pl proportion. Similarly, plagioclase proportion is increased by *f*O<sub>2</sub>. On this basis we are currently exploring additional pressures and *f*O<sub>2</sub> conditions which could drive derivative liquids toward the desired field.

In summary, experiments have evidenced at least one way to produce peralkaline liquids from near-metaluminous sources, via a mechanism we have termed the clinopyroxene effect, owing to the role played by this mineral (Scaillet and Macdonald, 2003) and which heavily relies on prevailing redox conditions. It is important to note that the chemical fractionation trend in Olkaria experiments runs counter the common evolutionary paths observed in intermediate to silicic series, notably in arc settings, in which fractionation proceeds at decreasing Fe and increasing Si contents. If such a trend of fractionation toward heavier melts is a common feature to peralkaline series, then it may have important fluid dynamical implications which remain to be fully explored. On the other hand, we have been so far unsuccessful in providing an experimental basis to the so-called plagioclase effect. We hope to be in position to either validate or invalidate this hypothesis in the near future.

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