

## Kinetics of liquid immiscibility in the system $K_2O$ - $CaO$ - $FeO$ - $Al_2O_3$ - $SiO_2$

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Our previous experiments on natural ferrobasic liquids showed that silicate liquid immiscibility may be seriously hampered by slow kinetics, metastable crystallization of tridymite, and the formation of sub-micron immiscible emulsions. Here we present new experiments on three synthetic compositions in the system  $K_2O$ - $CaO$ - $FeO$ - $Al_2O_3$ - $SiO_2$ . Two of the selected compositions lie inside the known miscibility gaps on the joins fayalite-orthoclase-silica and fayalite-hedenbergite-orthoclase-silica. The third composition lies on the anorthite-fayalite cotectic, well outside of known regions of stable or metastable liquid immiscibility. The charges in sealed Fe containers were first kept for 24 hours at a constant super-liquidus temperature, and quenched. Then, they were rapidly re-heated to the same temperature, and subjected to in situ centrifugation for 4 hours under acceleration of 1000 g. The aim of centrifugation was to distinguish between sub-liquidus emulsions due to quench, and those that may have formed by stable, super-liquidus immiscibility. The final glasses were studied by electron microprobe and transmission electron microscopy (TEM).

High-temperature super-liquidus emulsions formed in all the three compositions. The emulsions showed a remarkable stability, and did not completely break during centrifugation. Phase separation appears to be the fastest in the Ca-free composition on the fayalite-orthoclase-silica join. Here individual droplets readily grow to sizes of dozens and hundreds of microns, and merge to continuous liquid pools. The growth, coalescence and settling of droplets are significantly slower in the Ca-bearing fayalite-hedenbergite-orthoclase-silica composition. However, the most interesting and unexpected result was the formation of very fine, sub-micron emulsion in the composition on the anorthite-fayalite cotectic, where immiscibility had never been reported. The emulsion quenched to optically transparent glass, and could be revealed only by high-temperature centrifugation, electron microprobe profiles, and TEM.

Our results imply that the kinetics of silicate liquid immiscibility strongly depends on melt composition and viscosity. In some compositions, immiscibility may not develop beyond sub-micron scale for hours or days, and can be overlooked in conventional static experiments. If actual regions of silicate immiscibility are broader than presently thought, the petrogenetic role of immiscibility should be also revisited. In nature, large, slowly cooling magma chambers appear to offer enough time, and the best conditions for a full development of silicate liquid immiscibility.

## Molecular and isotopic biogeochemistry of Neoproterozoic sediments in the Rio de la Plata Craton

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The Upper Ediacaran Arroyo del Soldado group (ASG) in Uruguay and Corumbá group (CG) in SW-Brazil were deposited on the same passive continental margin of the Rio de la Plata Craton. They contain a largely unmetamorphosed sedimentary sequence of alternating siliciclastic and carbonate rocks, that have been investigated by inorganic and organic geochemical methods in order to get new insight about changes in climate and chemistry of oceans during the Neoproterozoic in SW-Gondwana.

We report isotopic data from carbonates ( $\delta^{13}C_{carb}$  and  $\delta^{18}O$ ) and associated organic carbon ( $\delta^{13}C_{ker}$  and  $\delta^{15}N_{ker}$ ), together with hydrocarbon distribution and concentrations of major, trace and rare earth elements (REE). The  $\delta^{13}C_{carb}$  values display coeval excursions in the two groups (ASG, CG) and range from -5.7 to 5.7‰. Dolostones from the Bocaina Formation in CG show the lowest  $\delta^{13}C_{carb}$  values, a typical signature of cap carbonates worldwide. The  $\delta^{13}C_{ker}$  values varying from -26.4 to -22.8‰ in CG and from -27.4 to -12‰ in the ASG reflect variations in the primary composition of organic matter as well as in the productivity rate during deposition. The  $\delta^{15}N_{ker}$  values in the CG samples range between -3.3 to -3.1‰, suggesting a primary contribution of cyanobacteria. More positive  $\delta^{15}N_{ker}$  values (1.8 to 5.2‰) in the ASG samples reflect most probably a higher planktonic contribution. Positive  $\delta^{13}C$  and  $\Delta^{13}C_{carb-ker}$  excursions, higher concentrations of redox sensitive elements (Mn, Fe, U and V), REE, and variations in the Ce anomaly in dark organic limestones of both groups can be explained by an increased bioproductivity and preservation of organic carbon at unusually high rates of sedimentation.

The main resolvable compounds in the gas chromatograms of the hydrocarbon saturated fraction are *n*-alkanes in the  $C_{12-30}$  (maxima at  $C_{21}$ ) and  $C_{14-35}$  (maxima at  $C_{26}$ ) ranges for CG and ASG samples respectively, in both cases with no odd-even predominance. Most samples have a hump of unresolved complex mixture in the  $C_{17-30}$  range. The predominance of  $C_{>18}$  of *n*-alkanes in the ASG samples confirm a marine planktonic input. The biomarker distribution (extended  $C_{29}$  to  $C_{34}$  hopanes, steranes) in the organic limestones of the CG are diagnostic for not strictly anaerobic bacteria and a diverse community of algae.