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1100°C tightly constrain the invariant point in T- $X_{Al}$  or P- $X_{Al}$  space. Analysis of the phase relations indicates that titanite solid solutions coexisting with rutile are always low in  $X_{Al}$ , whereas the maximum  $X_{Al}$  of titanite solid solution occurs with fluorite and either anorthite or  $Al_2SiO_5$ . These results demonstrate the influence of the coexisting mineral assemblage rather than the P-T conditions on the composition of titanite solid solutions.

### ASSESSMENT OF TEMPERATURE GRADIENTS IN MULTI-ANVIL ASSEMBLIES USING SPINEL GROWTH KINETICS

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Accurate measurements of axial and radial temperature distributions in high-pressure cells are a requirement for optimising assembly designs and constraining maximum sample volumes. Recently, Watson et al. (2002) presented an empirical equation linking the thickness of a  $MgAl_2O_4$  spinel layer growing at the interface between widely used  $MgO$  and  $Al_2O_3$  assembly pieces to pressure ( $P$ ), temperature ( $T$ ), and experimental duration ( $t$ ). Their equation, based on around 45 piston cylinder experiments at  $P$  up to 4 GPa and  $T$  up to 2250 K, can be inverted to calculate the temperature in different parts of high-pressure assemblies if  $P$ ,  $t$  and layer thickness are known.

We extended the  $PT$  range of this parametrisation to 16 GPa and 2250 K, using a multi-anvil press with 18/11 and 8/3 pressure cells, and high-resolution X-ray maps to determine spinel layer thicknesses. Our model, which deviates slightly from the Watson et al. (2002) lower-pressure parametrisation, can be used to assess thermal gradients in these common assemblies. At 6 GPa and 2123 K, axial  $T$  in the 18/11 assembly remains constant over a length of 4 mm when untapered graphite heaters are used.  $T$  decreases parabolically with axial distance from the edges of this 'hot spot'. The radial gradient is small (on the order of 30 K/mm distance from the center of the assembly). At 13-16 GPa in the 8/3 assembly with a rhenium foil heater, the hot spot is around 1 mm in length.  $T$  gradients outside this hot spot are large: 1 mm from the assembly center  $T$  has decreased by around 150 K.

Watson EB, Wark DA, Price JD & Van Orman JA, *Contrib. Mineral. Petrol.* (2002).

### MAGMATIC HYDROSALINE MELTS: EXAMPLES OF GRANITIC PEGMATITES AND NATROCARBONATITIC LAVAS

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Topology of some silicate-salt-water systems, such as Albite -  $NaCl - H_2O$ , or Albite -  $Na_2CO_3 - H_2O$  (Koster van Groos and Wyllie, 1968, 1969) shows that three immiscible fluids: aluminosilicate melt, hydrosaline melt and low-salinity aqueous fluid can stably coexist over a broad range of pressures and temperatures. The existence of three-fluid immiscibility in natural

magmatic systems is supported by numerous studies of melt and fluid inclusions (Roedder, 1992). Recent years have seen a growing interest in magmatic hydrosaline melts and their ore-forming capacity (e.g., Heinrich et al., 1999). However, despite the success of melt inclusion studies there was little progress in experimental characterisation of hydrosaline melts and almost no constraints on three-fluid element partitioning.

Hydrosaline melts may hold clues to understanding the most unusual and enigmatic igneous rocks: granitic pegmatites and natrocarbonatitic lavas. Our recent experimental study of B-, F- and P-rich peraluminous pegmatitic composition confirmed the formation of immiscible boro-alumino-fluoride melt in equilibrium with aluminosilicate melt and low-density aqueous fluid. Three-fluid immiscibility has been observed directly in hydrothermal diamond-anvil cells and in products of rapid-quench experiments in cold-seal pressure vessels at 0.1-0.4 GPa and 500-900°C. Immiscibility occurs at moderate concentrations of  $B_2O_3$ ,  $P_2O_5$  and F (each at about 3-5 weight percent) achievable in some types of pegmatites. Al, F, B and Na partition strongly to hydrosaline liquid, while P and K stay in aluminosilicate melt.

Dry silicate-carbonate liquid immiscibility is a broadly accepted mechanism explaining the origin of the unique natrocarbonatitic eruptions at the Oldoinyo Lengai (Tanzania). Detailed analysis reveals, however, significant discrepancies between experimental constraints on the two-liquid major and trace element partitioning and geochemical characteristics of natural natrocarbonatites (Nielsen and Veksler, in press). We believe that natrocarbonatitic lavas are likely to represent dried residues of originally water-bearing hydrosaline carbonatitic fluids.

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Nielsen TFD & Veksler IV, *Contrib. Mineral. Petrol.*, in press

### KINETICS OF MULLITE CRISTALLIZATION FROM NEUTRON THERMODIFFRACTOMETRY

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#### 1. Introduction.

The sequence of phases development leading the mullite formation during thermal treatment of its amorphous powder precursors, was followed by neutron powder thermodiffractometry. In this experiments, the role played by the Al-Si amorphous in the crystallization of the spinel precursor phase and its effects in the kinetics and mechanisms of the mullite formation, has been analysed as a function of the temperature (Villar et al, 2000).

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### 2. Experimental.

Amorphous precursor powders with stoichiometric mullite composition were heated up to 1700 °C by using the HTF in vacuum conditions at the E2 powder diffractometer. To test the possibility of reaction between the sample and the container, two different sample holders made from V and Pt were used.

The kinetics of phase transformation vs. temperature was obtained from the sequential refinement of the profiles by using the FullProf program [1] with a three-phase model. Estimation of the wt% fraction between the amorphous and crystalline phase was made from the integrated intensity of the whole background. Further treatment of the structural evolution of the amorphous phase was made by using reverse Montecarlo and Percus-Yevick models (Gago-Duport et al. 1995).

### 3. Results and discussion.

Starting from the amorphous precursor, a first crystallization of an Al-Si spinel-like phase takes place around 900°C (S.G. Fd3 m.  $a=7.79 \text{ \AA}$ ).

The mullite crystallization starts at 900°C. as is marked by the appearance of the (120) reflection. Both phases coexist until the temperature of 1275°C, from which the intensities corresponding to the reflections of the cubic spinel phase start to decrease. Finally, at 1400°C the only crystalline remaining phase in the sample is mullite.

One fact of interest is that the crystallization of mullite did not induce modifications in the intensities of the previously formed spinel phase at the first stages. Furthermore, every crystallization process is preceded of noticeable inflexions of the general shape and intensity of the background profile which can be connected with structural transformations in the amorphous Al-Si precursor during the nucleation of the crystalline phases.

This indicates that the crystallization of mullite and its precursor, spinel, results from independent nucleation events, both taken place directly by structural rearrangement of the amorphous phase.

Finally, a second relevant aspect concerns with the way of disappearance of the spinel phase at high temperatures. The kinetic analysis performed by the profile refinements shows that the intensity decrease of the spinel reflections is also related with the background modifications (Villar, 2000). This fact suggests that an amorphous-mediated transformation occurs by solid-state diffusion of the Al-Si in the spinel to the amorphous phase, with further recrystallization in the stable form of mullite (Gerardin et al, 1994)

These results indicate that, instead a polymorphic transformation from their precursor phases, the crystallization of mullite is a consequence of a direct nucleation followed of a solid-state diffusion and recrystallization processes where the amorphous phase plays a significative role.

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### EXPERIMENTAL DETERMINATION OF THE LIQUID LINE OF DESCENT OF ANHYDROUS THOLEIITIC MAGMAS AT 1.0 GPa

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Tholeiitic magmas are the most common eruptive products, which differentiate in deep-seated magma chambers ponding at the crust-mantle-boundary. The goal of this study is to quantify the liquid line of descent of dry mantle-derived tholeiitic magmas at pressures of 1.0 GPa.

As starting material we chose a mixture of synthetic oxides, fayalite, K-feldspar and NaSiO<sub>3</sub>, which corresponds to an experimentally produced liquid that was in equilibrium with a lherzolite mantle at 1.5 GPa and 1350°C (Hirose and Kushiro, 1993). The finely ground starting material was filled into a 2.6 mm OD graphite container, which was placed into a 3.0 mm OD platinum-capsule welded shut to prevent iron loss to the capsule and to fix the fO<sub>2</sub> at the C-CO<sub>2</sub> equilibrium. For the experiments a piston-cylinder-apparatus (Boyd-England-type), NaCl-Pyrex-MgO-Assemblies and Pt-Pt<sub>90</sub>Rh<sub>10</sub>-thermocouples were used. All experiments simulated equilibrium crystallization at 1.0 GPa.

In a first series of experiments olivine (ol) and Cr-spinel (spi) crystallized at 1270°C followed by clinopyroxene (cpx) at 1240°C. At 1210°C ol disappeared and orthopyroxene (opx) crystallized with cpx and Cr-spi. At 1180°C two pyroxenes but no spinel were present. Between 1150 and 1060°C cpx, opx and Al-spi represented the solid phases. No plagioclase (plg) occurred in this series.

In a second series of experiments 0.5 wt% of pure anorthite seeds were added to the starting material in order to test an eventual feldspar nucleation problem. In this series ol disappeared at 1180°C where opx, cpx but no spi crystallized. At 1150°C the solid products were cpx, opx and Al-spi. Cpx, opx, plg and Al-spi are the solid phases at 1120°C and 1090°C. These solid products represent ultramafic to mafic cumulates like dunites, wherlites, websterites and gabbronorites, which are common in plutonic rocks of the lower crust (e.g. layered series of the Ivrea-Zone, Rivalenti et al., 1981).

To understand the role of differentiation mechanisms of tholeiitic magmas at high pressure fractional crystallization experiments have been initiated.

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### NANOTEXTURES OF LASER-HEATED BIOTITES

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Chloritized biotites have been laser-heated according to four heating steps (laser power of 0.3, 0.7, 1.2, 2.2 W, corresponding to approximately 600, 810, 940, 1080°C, respectively; 2 min/step followed by 3 min of pumping out). Samples heated up to 600, 810, 940 and 1080°C have been investigated by high resolution TEM, in order to understand the structural and chemical transformation of biotite and interlayered chlorite. Most important results are: a) 600°C: biotite crystallinity is lower than in the untreated sample, reasonably due to dehydration processes. Chlorite breakdown is almost completed. b) 810°C: occurrence of diffuse delamination, 10-100 nm thick. Chlorite breakdown products start to crystallize. Main phases are spinels with variable composition, olivines and amorphous silica, occurring as irregular domains 10-20 nm in size, within the poorly crystalline biotite. c) 940°C: delamination is still present but it is reduced. Biotite is more crystalline than in previous sample. The chlorite breakdown products (olivines and spinels) form larger crystalline grains, typically elongated parallel to biotite (001). d) 1080°C: biotite (reasonably, oxybiotite) is characterized by higher crystallinity with respect to both treated and untreated samples, due to advanced structural annealing. EDS analyses performed on pure biotite domains are completely similar to those of the untreated biotite, thus indicating that biotite thermal transformation (i.e., dehydration followed by annealing at high temperature) was essentially isochemical. Olivine and spinels are hosted within perfectly euhedral negative crystals and show topotactic relation with the host biotite (thus, with the original chlorite): in particular [111]Spl parallel to [001]Bt(chl) and [100]Ol parallel to [001]Bt(chl). This evidence suggests that the crystallization of new phases is strongly influenced by the close packing of oxygens in the layer silicates; in particular the oxygen network of chlorite is inherited by its breakdown products.

### STRUCTURE AND RHEOLOGY OF PERALUMINOUS MELTS: THE EFFECT OF Fe<sub>2</sub>O<sub>3</sub>

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The Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system is used to model a large number of petrological processes. But even in this simple system there are anomalous changes in rheology as a function of composition. It has been previously shown for sodium-aluminosilicate melts that, at a constant temperature and constant SiO<sub>2</sub> content, there is a shallow maximum in viscosity in the vicinity of the subaluminous join. This maximum occurs within the peraluminous field, suggesting the presence of triclusters consisting of one aluminate and two silicate tetrahedra.

The viscosity of a range of Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub> compositions with 67 mol% SiO<sub>2</sub> and 0.60 > Na/(Na+Al) > 0.35, has been determined using the micro-penetration technique in the 8 < (log<sub>10</sub> Pa s) < 14 range. For these melts, at a temperature of 1050K, viscosity abruptly increases by 6.5 log<sub>10</sub> Pa s from an almost composition independent low viscosity for peralkaline compositions, to a composition independent viscosity as the melt composition becomes increasingly peraluminous. Thus, the shallow maximum in viscosity previously observed appears to be a plateau in viscosity for peraluminous composition Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> melts. The activation energy for viscous flow also changes dramatically as a function of melt composition; increasing from ~480 kJ mol<sup>-1</sup> for the peralkaline compositions, to ~630 kJ mol<sup>-1</sup> for the peraluminous compositions. This suggests that the change in melt structure due to the change in Na:Al has a dramatic effect on the flow mechanism of the melt.

The substitution of Fe<sub>2</sub>O<sub>3</sub> for up to 5% of the Al<sub>2</sub>O<sub>3</sub> in this system results in a decrease in viscosity. The activation energy for viscous flow for the peraluminous composition melts is decreased by ~20% upon the substitution of Fe<sub>2</sub>O<sub>3</sub> for Al<sub>2</sub>O<sub>3</sub>; but no change in activation energy is observed for the peralkaline compositions.

### TEXTURAL DEVELOPMENT OF DEHYDRATION-MELTING IN AMPHIBOLITE AT 2.0 GPa AND 950°: EFFECT OF TIME

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We have carried out the dehydration-melting of a natural amphibolite (56vol.% hornblende, 44vol.% plagioclase), in multi-anvil apparatus, experiments at 2.0 GPa and 950° for 1-170 hours. The samples are put into graphite capsules, which are sealed in gold capsules. As the annealing time less than 4 hours, Liquid and garnet appeared in the boundary of plagioclase and hornblende, which indicates this reaction: Hb + Pl — Liquid + Gt. In the mean time, two other reactions took place: Hb — Cpx + H<sub>2</sub>O and Pl — Ky + Na-Cpx + SiO<sub>2</sub>. Melting dominated by the growth of clinopyroxene and garnet. Liquid interconnectivity is attained, as the annealing time is 7 hours, with only about 5% liquid. As the annealing time increasing (from 10 hours to 72hours), liquids increased rapidly along with the loss of plagioclase (Ky + Na-Cpx + SiO<sub>2</sub>). As annealing time in range of 72-170 hours, only garnet and clinopyroxene is the solidus mineral. Most garnets are around the clinopyroxene. Garnet is enriched in pyrope. Liquids enrich first in An and then in Ab. And liquids are always silica rich (60-70 wt.% SiO<sub>2</sub>), strongly peraluminous (2-5 wt.% normative corundum), very felsic (Mg + FeO\* + TiO<sub>2</sub> less than 4wt.%). It is likely that segregation of initial liquids could not only effectively remove incompatible trace elements but although left the Gt + Cpx + Na-Cpx + Ky + SiO<sub>2</sub> assemble during the transition from amphibolites-faces to eclogite-faces.