

## THERMODYNAMIC BEHAVIOR OF ANALCIME-LEUCITE ANALOGUE SYSTEMS

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Only very limited solid solution exists between natural analcime (NaAlSi<sub>3</sub>O<sub>8</sub>·H<sub>2</sub>O) and leucite (KAlSi<sub>3</sub>O<sub>8</sub>), nor can this series be metastably synthesized. In order to explore the thermodynamic behavior of this system, we have studied the chemical analogue systems analcime - Rb-leucite (RbAlSi<sub>3</sub>O<sub>8</sub>) and analcime - pollucite (CsAlSi<sub>3</sub>O<sub>8</sub>), where synthesis is indeed possible. Such systems also offered case studies of complete solid solution between hydrous and anhydrous end members involving structurally coupled water-alkali-vacancy substitutions, a type of thermodynamic "mixing" that to our knowledge has not been previously investigated. Data have been collected on a hydrothermally synthesized ten-member Rb-bearing series and also a ten-member Cs-bearing series. Unit-cell results based on room-temperature X-ray diffraction measurements display non-linear behavior as a function of composition, evidence of non-ideal thermodynamic behavior. Interestingly, however, the enthalpies of solution measured in 20.1 weight percent hydrofluoric acid at 50°C are continuous and linear functions of composition for both series. Non-ideality, therefore, is athermal in both cases. To conclude this project, we are in the process of characterizing the energetic effects of Al:Si non-stoichiometry in this system, given the substantial effects of such non-stoichiometry found in the nepheline-kalsilite system (Hovis & Roux, 1999).

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STABILITY AND PHASE RELATIONS OF Ca[ZnSi<sub>3</sub>]O<sub>8</sub>, A NEW PHASE WITH FELDSPAR STRUCTURE IN THE SYSTEM CaO-ZnO-SiO<sub>2</sub>

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Zinc-feldspar, Ca[ZnSi<sub>3</sub>]O<sub>8</sub>, - a new phase - is located within the system CaO-ZnO-SiO<sub>2</sub> together with hardystonite, willemite, quartz and petedunnite [1,2,3].

Zinc-feldspar was synthesised hydrothermally within 35 days from an oxide mixture at 600°C/0.7 GPa. Ca[ZnSi<sub>3</sub>]O<sub>8</sub> crystallises in spacegroup P-1, displaying lattice constants of a=8.121(1) Å, b=12.927(1) Å, c=7.206(1) Å, α=93.76(5)°, β=116.120(7)°, γ=84.368(7)°, V=675.7 Å<sup>3</sup>, Z=2. Zn and Si are ordered on tetrahedral sites [4]. The high similarity to the structure of low albite is striking.

The stability of zinc-feldspar is limited to higher temperatures by reaction (1) 4 zinc-feldspar = willemite + 2 hardystonite + 7 quartz. It has a negative slope in the P-T-field, which can be expressed by the equation P=2.797(0.325)-0.0031(0.0004)T(°C). Two further reactions were determined by reversed experiments: (2) willemite + 2 hardystonite + 3 quartz = 4 petedunnite and (3) zinc-feldspar = petedunnite + quartz. Equation (3) is a double degenerated reaction. The intersection of the reactions (1), (2) and (3) generates an invariant point at about 530°C/1.2 GPa [5]. Due to the stability relations of the

SiO<sub>2</sub> system, two further invariant points I(low-/high-quartz) and I(high-quartz/tridymite) are generated at 720°C/0.57 GPa and 896°C/0.016 GPa.

Generally ZnO is not included in feldspar analyses by electron microprobe. However, Zn-enriched feldspar can be observed in seams, Pb-Zn hydrothermal vein deposits and in slags of lead blast furnaces. Naturally grown feldspar contains up to 0.18 wt% ZnO. In addition appreciable amounts of BaO were analysed in natural feldspars, too, implying a Ba[ZnSi<sub>3</sub>]O<sub>8</sub> component beside Ca[ZnSi<sub>3</sub>]O<sub>8</sub>.

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## RARE EARTH ELEMENT PARTITIONING BETWEEN CaSi-PEROVSKITE AND Mg-SILICATES UNDER MANTLE CONDITIONS: COMPARISON WITH INCLUSIONS IN DIAMOND

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Mantle minerals found as inclusions in diamonds from São Luiz, Brazil contain a wide range of rare earth element (REE) concentrations with originally perovskite structured CaSiO<sub>3</sub> (CaSiPvk) being by far the most REE-phyllic phase (Harte *et al.*, 1999 and Hutchison *et al.*, 2000). This observation is consistent with previous experimental results using mantle compositions (Kato *et al.*, 1988) and measurements of analogous CaTiO<sub>3</sub> perovskite found in kimberlites (Mitchell and Reed, 1988). A systematic experimental framework of partitioning data between CaSiPvk and coexisting phases allowing better constraint of the details of depth and temperature of formation of the natural sample has however, yet to be constructed. Partitioning of 10 REE are thus being investigated, initially in the CMS system. Starting materials of diopside glass doped with 1000 ppm REE oxides and mixed with 10wt% each of ReO<sub>2</sub> to buffer fO<sub>2</sub> and PbO<sub>2</sub> flux, are being employed. Experiments on Stony Brook's USSA-2000 and the University of Arizona's Walker-style 1000 ton multi-anvil presses have been conducted at 16.5, 20 and 22 GPa with temperatures between 1400°C and 2200°C in order to crystallise CaSiPvk with ilmenite, garnet and perovskite structured Mg-silicates in addition to the CM phase. Results analysed by SIMS and EPMA show that with decreasing Ca content in the Mg silicate phase, partition coefficients with CaSiPvk increase significantly. Partitioning with MgSiPvk is particularly extreme, involving values approaching those found for natural Mg-silicates coexisting with CaSiPvk, corroborating their previously attributed lower mantle origin. Additionally, Ca content and REE partitioning of some São Luiz 'diopsides' (Hutchison, 1997) are consistent with results in the CM field suggesting that these samples may have formed as the CM phase. Further experiments are being carried out to constrain the effects of pressure and temperature within phase fields and investigate the effects of additional atomic components and oxygen fugacity.

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### STRUCTURAL EFFECT OF THE $YSiCa_{1-P}$ SUBSTITUTION IN HYDROXYLAPATITE: AN NMR STUDY

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We have synthesized hydrothermally at 650°C and 0.15 GPa, yttrium-bearing silico-phosphate apatites,  $Ca_{5-x}Y_x(PO_4)_{4-x}(SiO_4)_xOH$  with  $x = [0, 3]$ . In the apatite structure, Ca and Y atoms are 9-fold (site I) and 7-fold (site II) coordinated, P and Si atoms occupy a single tetrahedral site. The oxygen of the hydroxyl groups is surrounded by three atoms of the site II. The hexagonal unit-cell volume determined by XRPD on our synthetic products decreases from the phosphate to the silicate pole. Inspection of the diffraction-peak intensities indicates that Y atoms are preferentially partitioned into the site II. <sup>1</sup>H MAS NMR spectra show a single resonance at 0.2 ppm for hydroxylapatite. This line still appears in the silicate end-member where hydroxylapatite-like environments are therefore preserved for some OH groups. As expected, the Y incorporation gives rise to new OH environments evidenced by two additional resonances centered around 1.5 and 4.9 ppm. <sup>31</sup>P MAS NMR spectrum of hydroxylapatite shows a single line at 2.8 ppm. For intermediate compositions, a broader line occurs at 1.7 ppm presumably due to the proximity of yttrium. In the heteronuclear <sup>1</sup>H-<sup>31</sup>P correlation maps, the proton lines at 0.2 ppm and 1.5 ppm are correlated to the <sup>31</sup>P lines at 2.8 ppm and 1.7 ppm, respectively. These resonances correspond to protons which have phosphate anions in their neighbourhood. Adversely, the proton line at 4.9 ppm is not correlated to any <sup>31</sup>P lines. It may correspond to protons surrounded by silicate anions. Assuming that the charge balance (YSi = CaP) is locally achieved, these protons should also be close to yttrium atoms. FTIR shows the usual hydroxylapatite band at 3572 cm<sup>-1</sup> and a broad band at around 3544 cm<sup>-1</sup>. Proton spectra (FTIR and <sup>1</sup>H NMR) display a global intensity decrease from the phosphate pole to the silicate pole. This result suggests that protons may charge-balance part of the Ca-Y replacement.

### QUANTITATIVE MEASUREMENT OF HYDROGEN IN MANTLE XENOLITHS, EQUILIBRIUM CONCENTRATIONS AND PARTITION COEFFICIENTS

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Quantitative measurement of hydrogen content in single crystals can be determined by polarised infrared spectroscopy using calibrated extinction coefficients (Bell *et al.*, 1995; Libowitzky and Rossman, 1997). However, such techniques necessitate to record polarised infrared spectra in at least 2 perpendicular crystallographic orientations and three different polarised directions. Such procedure is difficult to apply to polycrystalline mantle xenoliths with small grain size. An alternative possibility is to perform a single infrared analysis on each individual crystal of the xenolith and to build an averaged infrared spectra representative of each mineral phase present in the xenolith.

We report results from infrared analyses performed on a xenolith from Kilbourne Hole (New Mexico) recovered from about 50 km depth (1030°C, 1.7 GPa; Glücklich, 1992). Infrared profiles realised within single crystals and across grain boundaries show no hydrogen concentration gradient even at distances less than 10 microns from grain boundaries. In these conditions, the hydrogen content of each mineral phase can be assumed homogeneous and each phase is in equilibrium with the others. More than 100 analyses were recorded and averaged, allowing to measure the hydrogen content in olivine, enstatite and diopside and the partition coefficients of hydrogen F between these phases:

$$F_{\text{enstatite/olivine}} = 170 \text{ and } F_{\text{diopside/olivine}} = 360$$

The total amount of hydrogen transported by the xenolith is estimated to an equivalent of 100 ppm H<sub>2</sub>O. These results are compared to hydrogen solubility data obtained from high-pressure experiments performed on olivine, enstatite and diopside.

Xenoliths from different origins and the same origin but recovered from different depths are currently investigated.

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### HYDROGEN MOBILITY IN SINGLE CRYSTAL KAERSUTITE

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Experimental data on the kinetic of H-D exchange in amphiboles have been widely used to evaluate the rate of oxidation of mantle-derived amphibole xenoliths during their ascent towards the surface and to decipher on the possible variation in the oxidation state of mantle metasomatic fluids (Dyar *et al.*, 1993; King *et al.*, 1999). Unfortunately, previous experimental kinetic data have been measured on powder amphibole. This technique is highly dependent on the shape model used for individual grains and how the average grain size is determined (Graham *et al.*, 1984). It generally leads to large uncertainties on the diffusion coefficients determination. It also precludes any possibility to collect data on the anisotropy of hydrogen diffusion in single crystals.

H-D exchange experiments were performed between a gas and thin plates of kaersutite (40 to 80 microns thick) cut perpendicular to [010] and [001] directions. Data were collected in the temperature range of 600 and 900°C. Diffusion coefficients along [010] fitted to an Arrhenius function:

$$D \text{ (m}^2\text{/s)} = 2 \cdot 10^{-14} \exp(-104 \text{ kJ/mol}/RT)$$

give results slightly above, with comparable activation energy, to the average values deduced by Graham *et al.* (1984) for a model of grains with plate shape. However, preliminary data collected along [001] direction suggest that diffusion of hydrogen in amphibole is anisotropic. The rate of diffusion along [001] is around one order of magnitude faster than along [010] direction.

These data are used to simulate the dehydrogenation rate of single crystals kaersutite sampled from the mantle within the time scale of few hours to few days.

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