

## Goldschmidt Conference Abstracts 2006

### Crystal-chemical investigation of kalsilite from San Venanzo, Italy, using single-crystal X-ray diffraction and Raman spectroscopy

H. UCHIDA, R.T. DOWNS, H. YANG

Department of Geosciences, University of Arizona, USA ([uchida@geo.arizona.edu](mailto:uchida@geo.arizona.edu))

Kalsilite,  $\text{KAlSiO}_4$ , is an end-member of the ternary system,  $\text{NaAlSiO}_4$  (nepheline)- $\text{KAlSiO}_4$ - $\text{SiO}_2$ , which includes many important rock-forming minerals. Previous studies have provided several space groups for kalsilite:  $P6_322$  (Bannister and Hey, 1942),  $P6_3$  (Perrotta et al., 1965),  $P6_3mc$  (Dollase and Freeborn, 1977), and  $P31c$  (Cellai et al., 1997). In this study, a natural kalsilite,  $(\text{K}_{0.92}\text{Na}_{0.07})(\text{Al}_{0.93}\text{Fe}^{3+}_{0.04}\text{Si}_{1.03})\text{O}_4$ , from San Venanzo, Italy, was investigated with a Bruker X8 Apex CCD single-crystal X-ray diffractometer. The crystal is hexagonal with  $a = 5.1589(2) \text{ \AA}$ ,  $c = 8.6682(3) \text{ \AA}$ , and  $V = 199.79(13) \text{ \AA}^3$ . Weak diffuse scattering was observed along some strong reflections, but no twinning was detected. Observed systematic absences suggest possible space group  $P6_3$  or  $P6_322$ , but the intensity data point to  $P6_322$ . The structure refinements based on  $P6_322$  symmetry (25 variables, 585 reflections) with SHELX97 produced an  $R_1$  factor of 0.0260, compared to that of 0.0271 based on  $P6_3$  (43 variables, 1057 reflections). This study provides the first substantiated structure of kalsilite with its originally reported symmetry  $P6_322$ .

The  $P6_322$  structure of kalsilite is characterized by the disordering of both O1 and O2 atoms, with O1 on the  $6h$  (1/3 occupancy) and O2 on the  $12i$  (1/2 occupancy) positions, as a consequence of the rigid-body motion of the  $(\text{Si,Al})\text{O}_4$  group. While the small amount of Na occupies a site that is  $\sim 0.3 \text{ \AA}$  away from the K position, the Al and Si atoms occupy the same  $4f$  site. This observation agrees with the measured Raman spectrum, which exhibits a single strong Si–O–Si stretching peak at  $\sim 350 \text{ cm}^{-1}$ .

#### References

- Bannister, F.A., Hey, M.H., 1942. *Miner. Mag.* **26**, 218–224.  
Cellai, D., Bonazzi, P., Carpenter, M.A., 1997. *Am. Miner.* **82**, 276–279.  
Dollase, W.A., Freeborn, W.P., 1977. *Am. Miner.* **62**, 336–340.  
Perrotta, A.J., Smith, S.M., Smith, J.V., 1965. *Miner. Mag.* **35**, 588–595.

doi:10.1016/j.gca.2006.06.1267

### New experimental technique for $P$ – $V$ – $T$ measurements of crustal fluids around critical point

YOSHIHARU UCHIDA, KENSHIRO OTSUKI

Department of Geoenvironmental Science, Graduate School of Science, Tohoku University, Japan ([uchida@dges.tohoku.ac.jp](mailto:uchida@dges.tohoku.ac.jp); [otsuki@dges.tohoku.ac.jp](mailto:otsuki@dges.tohoku.ac.jp))

The equation of state (EOS) of crustal fluids ( $\text{H}_2\text{O}$ – $\text{CO}_2$ – $\text{NaCl}$ ) over the wide range of  $P$  and  $T$  is the most important for understanding geochemical processes. However, in the region  $P < 100 \text{ MPa}$  and  $350 \text{ }^\circ\text{C} < T < 600 \text{ }^\circ\text{C}$ , SUPCRT92 (Johnson et al., 1992) which is most available calculation program cannot estimate the thermodynamic properties of high salinity solution with high  $\text{CO}_2$  concentrations because of the effects of charged species. The EOS that is specified for high saline  $\text{H}_2\text{O}$ – $\text{CO}_2$ – $\text{NaCl}$  ( $>25 \text{ wt}\%$ ) systems has not been also established yet, because experiments have not been done successfully around the critical point.

Now we have developed a new apparatus; a mini-piston/cylinder system set in the pressure vessel of our tri-axial deformation apparatus.  $V$  is measured by monitoring the motion of the mini-piston, and  $T$  is measured by a thermocouple continuously and synchronously. This apparatus serves for the experiments on high saline crustal fluids with high  $\text{CO}_2$  concentrations under the conditions up to 200 MPa and 600  $^\circ\text{C}$ . We verified the performance of our apparatus by comparing our experimental data for pure water and  $\text{H}_2\text{O}$ –10 or 20 mol%  $\text{CO}_2$  with the calculated values from the preexisting EOS (Duan et al., 1995) over the  $P$ – $T$  conditions attainable. Our experimental data are consistent with preexisting EOS within accuracy of about 1%. Our innovative experimental technique will establish the EOS of any kind of crustal fluids in the near future.

#### References

- Duan, Z., Moller, N., Weare, J.H., 1995. *GCA* **59**, 2869–2882.  
Johnson, J.W., Oelkers, E.H., Helgeson, H.C., 1992. *Computers Geosci.* **18**, 986–990.

doi:10.1016/j.gca.2006.06.1268