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## MS14-P02

## NMR crystallography of beryl minerals at 9.4 T and 19.6 T

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The available description of the aluminosilicate beryl group of minerals suggests  $RX_3Al_2(Si_6O_{18}) \cdot H_2O$  as general formula, with beryl  $Be_3Al_2Si_6O_{18}$  (*P6/mcc*) and pezzottaite  $Cs(Be_2Li)Al_2Si_6O_{18}$  (*R-3c* or *R3c*) as end-members. It involves a wide diversity of intermediate chemical compositions because the structure can incorporate different alkali atoms in solid solution, located at channel R site and tetrahedral X sites, and  $H_2O$  molecules in the structural channel. Reciprocal-space techniques have resolved only average structures in the intermediate members, related to one of the two the ideal crystal structure of the end-members, and have difficulties in the study of water molecules. Here, high-resolution multinuclear NMR spectroscopy, leading to  $^{29}Si$ ,  $^{27}Al$ ,  $^9Be$ ,  $^{133}Cs$ ,  $^7Li$ ,  $^{23}Na$  and  $^1H$  spectra at 9.4 T as well as  $^{27}Al$  and  $^9Be$  spectra at 19.6 T, has been used to investigate the short- and medium-range structures in nine specimens along the solid solution of this group. The  $^1H$  NMR SP and CP experiments suggest that hydrogen atoms are actually as OH groups for compensation of local charge, instead of water molecules which were detected in very low concentration. The structural description by reciprocal-space techniques and NMR coincides only in the alkali-free perfectly long-range ordered *P6/mcc* beryl end-member, which in fact is extremely rare in Nature, having one tetrahedral site for Si atoms, one octahedral site for Al atoms, and one tetrahedral site for Be atoms. However a tectosilicate description seems more appropriated that a cyclosilicate classification from the values of the  $^{29}Si$  chemical shifts, as Be and Si atoms form a  $Q^4$  configuration. The most common mineral is alkali-rich beryl having a crystal structure with lower local symmetry than the ideal average hexagonal structure, with at least two sites for Si atoms, four sites for Be atoms, two R sites and two X sites for Li atoms, two R sites for Na atoms, one R site Cs atoms, and two types of OH groups. The NMR data of pezzottaite indicate six tetrahedral sites for Si atoms, two octahedral sites for Al atoms, one tetrahedral site for Be atoms, two R sites and two X sites for Li atoms, three R sites for Cs atoms, and two types of OH groups with one of them different from that of beryl. The lack of resolving power of diffraction techniques to resolve the structural detail of non stoichiometric beryl is similar to that found in order-disorder series of K-feldspars (Sánchez-Muñoz et al. 2013).

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**MS14-P03**

## Application of the full-symmetry Patterson sum-function to the solution of complex cluster-based minerals from powder diffraction data

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Often, poorly growing minerals are based on self-assembly of metal clusters e.g. via H bond networks [1]. If the unit cell and the space group symmetry of these compounds can be estimated from the powder diffraction pattern, then this information can be used 1) to extract the cluster intensities from the pattern 2) to strengthen the Patterson sum-function application ( $S_p$ ) [2] by reducing the number of phases to be refined (the  $S_p$ -FT algorithm is implemented in the XLENS\_PD6 code retrievable from <https://departments.icmab.es/crystallography/software>). Unlike direct-space structure solution methods, the  $S_p$ -FT algorithm is especially well-suited for crystal structures containing cations with irregular or unpredictable coordination polyhedra or when some structural disorder is present. Although this algorithm was initially developed for organic compounds, it will be shown that it is also suitable for the location of light atoms in the presence of a large number of heavy atoms.

In those cases where the unit cell cannot be found directly from the powder pattern, electron diffraction tomography (EDT) constitutes an alternative way of solving the crystal structure. However, its efficiency decreases if the sample is sensitive to vacuum induced dehydration. It will be shown that even in such unfavorable circumstances the information provided by EDT is complementary to that of PD and can be used to advantage by the  $S_p$ -FT algorithm. This will be illustrated on the solution of the unknown crystal structure of decrespignyite-(Y), a new complex copper yttrium rare-earth carbonate chloride hydrate from Paratoo (South Australia) [3].

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