# Supplementary Material 1

# ****“Structural State of Rare Earth Elements in Eudialyte Group Minerals”****

Borst, A.M.1, Finch, A.A.1, Friis, H.2, Horsburgh N.J.1, Gamaletsos, P.N.3,4, Goettlicher, J., Steininger, R.5, Geraki, T6

*Mineralogical Magazine, 2019*

1) School of Earth & Environmental Sciences, University of St Andrews, North Street, St Andrews, United Kingdom

2) Natural History Museum, University of Oslo, Oslo, Postboks 1172, Blindern

0318 Oslo, Norway

3) Department of Materials Engineering, KU Leuven, Kasteelpark Arenberg 44, 3001 Leuven, Belgium

4) Center for Electron Nanoscopy, Technical University of Denmark, 2800 Kongens Lyngby, Denmark

5) Institute for Photon Science and Synchrotron Radiation, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany

6) Science Division, Diamond Light Source, Harwell Science and Innovation Campus, Didcot, United Kingdom

**S1.1 Compositional analyses of EGM samples**

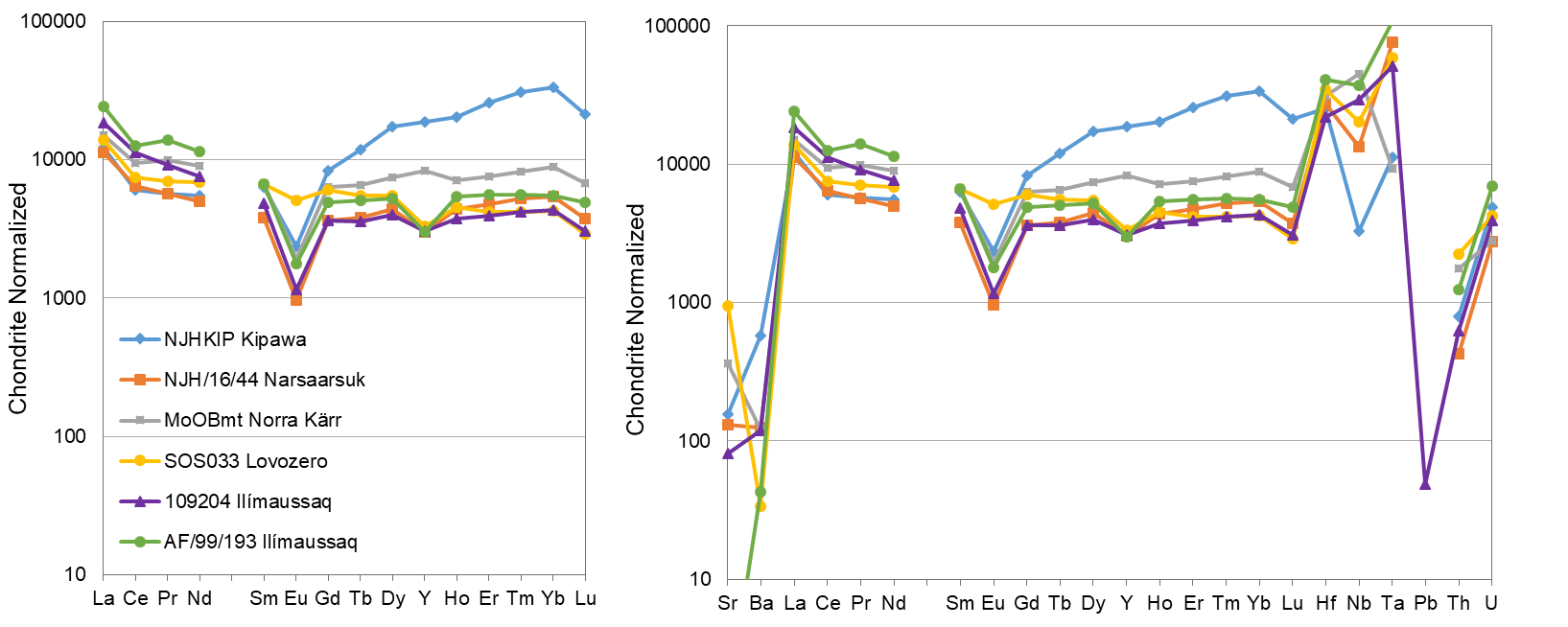
***S1.1.1 Major and trace element analyses***

Major element compositions were measured by wavelength dispersive spectroscopy using a CAMECA SX100 electron probe micro-analyzer (EPMA) at the University of Edinburgh, United Kingdom. Eudialyte compositions were measured using an acceleration voltage of 15 kV and larger beam size of 15 µm to avoid loss of volatile elements. Na, Cl, Zr and Si were measured first to avoid beam damage effects, and Cl measured on two spectrometers to maximize signal. The beam current was set to 4 nA for major elements (Na, Si, K, Ca, Fe, Mn and Zr) and 100 nA for minor elements (Mg, Al, Cl, Y, Nb, La, Ce, Nd, Ta, Hf, Ti). Depending on abundance, counting times varied from 10 to 60 seconds on peak, with half that off peak. Calibration standards were jadeite (Na lα), wollastonite (Ca kα, Si kα), orthoclase (K kα), fayalite (Fe kα), PuMn (Mn kα), zircon (Zr lα), spinel (Mg kα, Al kα), NaCl (Cl kα), synthetic REE-phosphates (La lα, Ce lβ, Nd lβ,Y lα), Nb metal (Nb lα), Ta metal (Ta lα), rutile (Ti kα) and hafnon (Hf lα). Formula units are calculated on the basis of Si+Al+Zr+Hf+Ti+Nb+Al = 29. EGM endmember components are calculated by sequentially filling the structural sites in a pre-defined order, using the calculation sheet provided by Pfaff et al. (2010), following the method of Johnsen and Grice (1999). This approach fills the stable M(3)M(4)Z3 part of the structure first, followed by the more variable M2, M1 and N sites. All REE are automatically assigned to the M1 site unless the sum of Ca + REE exceeds 6. Excess Ca and REE are subsequently assigned to the N site. The possibility that the heavy and light REE may occupy different structural sites is generally not considered in these schemes.

Trace elements were measured by Laser Ablation Inductively coupled Mass Spectroscopy at the School of Earth and Environmental Sciences, University of St Andrews, United Kingdom. The system comprises an UP213 New Wave Laser system attached to a Thermo X'Series II ICPMS. Data was processed offline using Pepita software (Dunkl et al, 2008), using Ca and Ce as internal standard elements.

***S1.1.2 Results***

Chondrite normalized (Palme & O’Neill, 2003) REE patterns for the EGM samples studied are shown in Fig S1. Eudialyte Group Mineral compositional data are presented in Table S2. Endmembers components calculated using the sheet of Pfaff *et al*. (2010) show a dominance of eudialyte components, followed by kentbrooksite, in most EGM samples. Eudialyte components range from 0.90 (out of 1) in EGM from Ilímaussaq (kakortokite Unit 0, Borst *et al.,* 2018) to 0.41-0.35 in the Kipawa sample. The latter further comprises 0.17 parts kentbrooksite, and 0.42 parts alluaivite, reflecting low Fe and high Ca and Y contents, which leads to some Na being placed on the M2 site during the site assignment procedure. Of all samples, the Kipawa sample has the most HREE enriched profile (Fig S2). Endmember calculations suggest that the Lovozero sample is a (Mn,Ca)-ordered EGM variety, where a proportion of M1 octahedra are occupied by Mn instead of Ca (Table S2). The increasing replacement of Ca by Mn in the six-membered rings leads to disappearance of the *m* plane (perpendicular to the c-axis), reducing the symmetry for raslakite, oneillite and (Mn,Ca)-ordered eudialyte to the R3 space group. These are all part of the oneillite-subgroup (Rastsvetaeva, 2007). How much Mn occupies the M1 sites in the Lovozero sample, and whether it represents a raslakite, oneillite or (Mn,Ca)-ordered eudialyte component, cannot be determined without crystallographic data. Hence, the endmember calculation for this sample by the sheet of Pfaff *et al.* (2010) is inadequate (reflected in sum of components >1). Nevertheless, to illustrate how the partitioning behaviour for the REE changes, theoretically, when Mn or Fe ideally occupies one of the M1-subsites (oneillite subgroup), we have included Mn-dominated M1a/b site parameters in the calculation of partitioning models (main text, Figure 9). The lattice strain theory models suggest that EGM members that have a preferred site for octahedrally coordinated Mn on one of its M1 subsites will show a significant increase in the bulk mineral partition coefficients for HREE, with the highest partition coefficients centering at Lu for Mn dominated M1a/b sites, as opposed to a preference for Pr and Nd for Ca-dominated sites.

**

***Fig S1.1.*** *Chondrite normalized (Palme & O’Neill, 2003) Rare Earth element patterns and trace element patterns for analysed eudialyte group samples.*

**S1.2 NdPO4 synthesis**

Monazite-(Nd) doped with 5 mol.% yttrium was synthesized at the School of Earth and Environmental Science, University of St Andrews. Reagents (Nd2O3, Y2O3 and NH4H2PO4 powders) were weighed to stoichiometric proportions and thoroughly mixed and ground in an agate mortar for 30 minutes, ensuring all reagents were washed out of the weighing trays using ethanol. Homogenized powders were pressed into pellets at 2 t/m2. The pellets were pre-heated at 500 °C for 3 hours, then reground and repressed, and re-heated twice for 12 hours at 1000 °C (following Friis (2009)). Repeated grinding and pressing between heating sessions acted to maximise chemical homogeneity and prevent the formation of YPO4-(Y) micro-domains within the monazite structure. Phase pure micro-crystallinity of the monazite-(Nd) structure was achieved after 24 hours of heating at °1000 C and confirmed by XRD.

**S1.3. SUL-X Beamline Details**

The X-ray beamline of the Laboratory for Environmental Studies (SUL-X beamline, Göttlicher et al. (2006)) at the KIT Karlsruhe Light Source (Karlsruhe Institute for Technology, Germany, formerly the ANKA Synchrotron Radiation Facility) operates at a 27 pole Wiggler radiation source, covering an energy range of 2.4 to 20 keV and using a fixed exit Si(111) double crystal monochromator cooled with liquid nitrogen, to provide an energy resolution of c. 1.5 x 10-4 (at 10 keV). The beam was pre-focused to an intermediate focus and then fully focused to the sample position using a Kirckpatrick Baez mirror system, to a beam size of 250 µm (horizontal) by 150 µm (vertical). Smaller beam sizes down to 50 x 50 µm2 were adjusted by decreasing slit widths at the intermediate focus. Spectra were measured in transmission and fluorescence using ionization chambers in front and behind the sample and a seven element Si(Li) solid state detector (Rayspec, former Gresham) for recording the corresponding fluorescence emission signals (Nd Lα1,2, Y Kα1,2). The first ionization chamber was used in both transmission and fluorescence modes for normalization of the absorption and fluorescence intensities.

Energy was calibrated to 6539 eV (first inflection point of Mn K XANES spectra of a Mn metal foil) for the Nd L3 edge spectra (Nd L3 edge 6208 eV) and to 17038 eV for the Y K-edge spectra (first inflection point of Y K XANES spectrum of Y metal foil). Because samples contain Ce and the Ce L2 edge (6164 eV) is just in front of the Nd L3 edge and Lβ1 fluorescence emission cannot be separated with a Si(Li) detector, the Ce L2 edge has been recorded together with Nd L3 edge scans to get additional information about Ce speciation. Higher harmonics for the low energy absorption edge measurements (Ce L2, Nd L3) and for the high energy absorption edge measurements (Y K) were cut by Si or Rh coated mirrors, respectively. XANES spectra were recorded in energy steps of 1 eV from –150 to –65 eV and of 0.4 eV from –65 to –20 eV across the edge (to include the Ce L2 edge), and with a k step of 0.05 from k 2.29 to k 7.8 (limited by the Pr L2 edge) (+20 to about +230, 6440; acquisition time factor 1xk0.5) above the edge, and for Y K edge in energy steps of 5 eV from –200 to –50 eV, of 2 eV from –50 to –20 eV prior to the edge, of 0.4 or 0.5 eV from –20 to +20 eV across the edge, and with a k step of 0.05 from k 2.29 to k 12 (+20 to about +540 eV; 17600 eV, acquisition time factor 0.44xk1).

**S1.4. Determination of S02 and refining coordination numbers in ARTEMIS**

The Artemis Demeter Perl software package (Ravel & Newville, 2005) was used for refinement of EXAFS data, in order to yield bond distances, coordination numbers and Debye-Waller factors. It is important to note that the coordination number (CN, or ‘degeneracy number’ in Artemis) is directly correlated to the amplitude reduction factor (S02) in the IFEFFIT program implemented in Artemis (Ravel & Newville, 2005, Rehr & Albers, 2000). Consequently, these two parameters cannot be refined independently. Determination of coordination numbers from EXAFS data is challenging due to e.g. statistical limitations of the fitting procedure, empirical effects of sample preparation, normalization and background extraction procedures and physical assumptions made about the absorbing atom (Ravel & Kelly, 2007). Nevertheless, CN can be approximated when the value for S02 is fixed, typically to a value of 1. Realistic values for S02 however may vary between 1 and 0.7 (Ravel & Kelly, 2007). Therefore a more accurate approach is to determine S02 from a well-identified standard with a known CN, measured under the same conditions as the samples, and assuming chemical transferability for S02. From the standard, S02 can be fitted while fixing the CN values to the ideal crystallographic value. When we do this for metallic yttrium foil (CN=12) a single shell fit yields an optimal S02 of 0.7 ± 0.1. This is on the low end of reasonable S02 values, which we interpret to reflect self-absorption and attenuation of the EXAFS signal due to Y-Y correlation (Fig. 4a). The latter was also observed in EXAFS spectra of Zr-Zr bonds in zirconia (Rush *et al.*, 2000). Since S02 is a parameter of the absorber and CN a parameter of the scatterer, S02 ­­can be refined more accurately from multiple shells with different scatterers (Ravel & Kelly, 2007). Therefore, a more suitable standard to determine S02 is Y2O3 where Y is surrounded by three single-scattering shells (6 Y, 6 O and 6 Y). Fits for these three paths with fixed coordination numbers yield S02 of 1.00 ± 0.18 (R-factor 0.024). The resulting bond distances agree well with the structural model of Santos *et al.* (2005) and the pattern is consistent with EXAFS data for cubic Y2O3 from Lazdins and Kuzmin (2015), giving credence to our approach and the use of an S02 valueof 1. Nevertheless, some degree of uncertainty on the exact value of S02 is inevitable, and hence CN numbers are fixed to the values derived from the structural model in the eudialyte sample.

**References**

Bevan, D., Strähle, J. & Greis, O. (1982). The crystal structure of tveitite, an ordered yttrofluorite mineral. J. *Solid State Chem*. **44**, 75-81.

Boatner, L. A. (2002). Synthesis, Structure, and Properties of Monazite, Pretulite, and Xenotime. *Rev. Miner. Geochem*. **48**, 87-121.

Cámara, F., Sokolova, E. & Hawthorne, F. (2011). From structure topology to chemical composition. XII. Titanium silicates: the crystal chemistry of rinkite, Na2Ca4REETi (Si2O7) 2OF3. *Mineral. Mag.* **75**, 2755-2774.

Dunkl, I., Mikes, T., Simon, K. & Von Eynatten, H. (2008). Brief introduction to the Windows program Pepita: data visualization, and reduction, outlier rejection, calculation of trace element ratios and concentrations from LAICPMS data. *Mineralogical Association of Canada*, Short Course, 40, pp.334-340

Dollase, W. (1971). Refinement of the crystal structures of epidote, allanite and hancockite. *Am. Min*. **56**, 447-464.

Finch, R., Kropf, A. & Hanchar, J. (2001). EXAFS Investigation of Rare Earth Elements in Synthetic Zircon. Eleventh Annual V. M. Goldschmidt Conference.

Friis, H. (2009). Luminescence spectroscopy of natural and synthetic REE-bearing minerals. PhD Thesis. *School of Geography and Geosciences*. St Andrews: University of St Andrews.

Göttlicher, J., R, S. and (2006), S.R. (2006) Combination of micro X-ray techniques: the synchrotron radiation laboratory for environmental studies at ANKA, 12th European Conference on X-Ray Spectrometry (EXRS 2006), Paris, France.

Hanchar, J. M., Finch, R. J., Hoskin, P. W., Watson, E. B., Cherniak, D. J. & Mariano, A. N. (2001). Rare earth elements in synthetic zircon: Part 1. Synthesis, and rare earth element and phosphorus doping. *Am. Mineral*. **86**, 667-680.

Hughes, J. M., Cameron, M. & Crowley, K. D. (1989). Structural variations in natural F, OH, and Cl apatites. *Am. Mineral*. **74**, 870-876.

Johnsen, O. & Grice, J. D. (1999). The crystal chemistry of the eudialyte group. *Can. Mineral.* **37**, 865-891.

Lazdins, K. & Kuzmin, A. (2015). Local structure and lattice dynamics of cubic Y2O3: an x-ray absorption spectroscopy study. *IOP Conference Series: Materials Science and Engineering*: IOP Publishing, 012031.

Mazzi, F. & Ungaretti, L. (1994). The crystal structure of vitusite from Ilímaussaq (South Greenland): Na3REE (PO4) 2. *Neues Jb. Mineral*. *Monatshefte* 49-66.

Moore, P. & Shen, J. (1983). Crystal structure of steenstrupine: a rod structure of unusual complexity. *Tschermaks Mineralogische und petrographische Mitteilungen* **31**, 47-67.

Ni, Y., Hughes, H. S. R. & Mariano, A. (1993). The atomic arrangement of bastnasite-(Ce), Ce (C03) F, and structural elements of synchysite-(Ce), rontgenite-(Ce), and parisite-(Ce). *Am. Miner.***78**, 415-418.

Ni, Y., Hughes, J. M. & Mariano, A. N. (1995). Crystal chemistry of the monazite and xenotime structures. *Am. Miner.* **80**, 21-26.

Noe, D. C., Hughes, J. M., Mariano, A. N., Drexler, J. W. & Kato, A. (1993). The crystal structure of monoclinic britholite-(Ce) and britholite-(Y). *Zeitschrift für Kristallographie-Crystalline Materials* 206, 233-246.

Pfaff, K., Wenzel, T., Schilling, J., Marks, M. & Markl, G. (2010). A fast and easy-to-use approach to cation site assignment for eudialyte group minerals. *Neues Jb. Miner.* **187**, 69-81.

Rastsvetaeva, R. (2007). Structural mineralogy of the eudialyte group: A review. *Crystall. Rep.* **52**, 47-64.

Ravel, B. & Kelly, S. (2007). The difficult chore of measuring coordination by EXAFS. *AIP Conference Proceedings*: AIP, 150-152.

Ravel, B. & Newville, M. (2005). ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT*. J. Synchrotron Radiat.* **12**, 537-541.

Rehr, J. J. & Albers, R. C. (2000). Theoretical approaches to x-ray absorption fine structure. *Reviews of modern physics* **72**, 621.

Rush, G. E., Chadwick, A. V., Kosacki, I. & Anderson, H. U. (2000). An EXAFS study of nanocrystalline yttrium stabilized cubic zirconia films and pure zirconia powders. *J. Physic. Chem. B* **104**, 9597-9606.

Santos, C., Strecker, K., Suzuki, P., Kycia, S., Silva, O. & Silva, C. (2005). Stabilization of α-SiAlONs using a rare-earth mixed oxide (RE2O3) as sintering additive. *Materials*