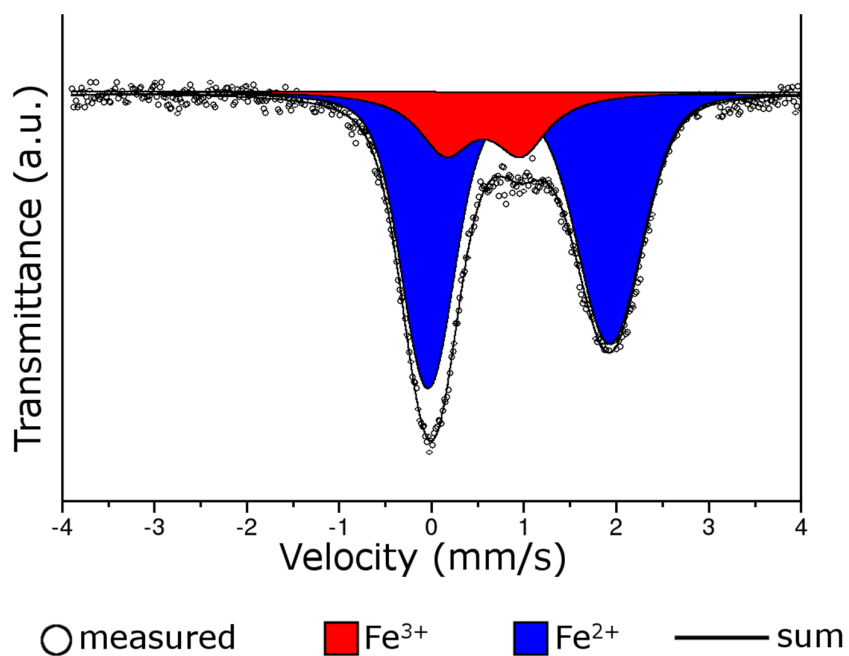## Appendix A

**Room-temperature Mössbauer spectrum of zirconolite**

Figure A1. Room-temperature Mössbauer spectrum of zirconolite

Table A1. Quantitative parameters of the Mössbauer spectrum of zirconolite from Fig. A1

Isomer shift	Quadrupole splitting	Full width	Area	Assignment
mm/s	mm/s	mm/s	%	
0.564	0.819	0.701	20.6	Fe^{3+}
0.949	1.967	0.226	79.4	Fe^{2+}

Appendix B

X-ray powder diffraction patterns of unannealed and thermally annealed zirconolite
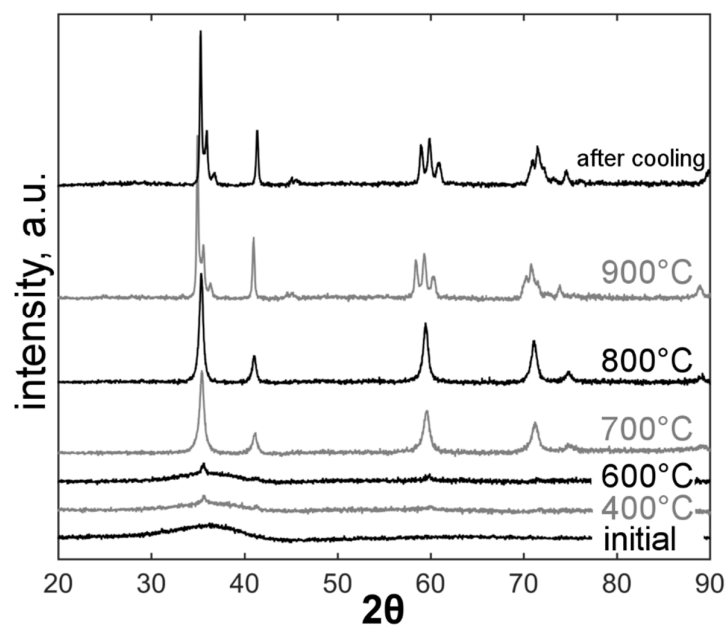
Figure B2. X-ray powder diffraction patterns of unannealed and thermally annealed zirconolite from the LPC. Variation of the diffraction patterns with increasing temperature due to recrystallisation of initially radiation-damaged mineral.

Appendix C

Estimation of iron oxidation state (X_{Fe3+}) or X_{Me3+} from other composition variables: X_{REE*} and X_{Me5+*}

The Equation 1, $X_{Me3+} = 2 - 2X_{REE} - 3X_{Me5+}$, introduced in the article, is **valid for a sort of zirconolite**, which can be expressed by formula $(Ca,REE)_2Zr_2(Ti,Me^{5+})_3(Me^{2+},Me^{3+})O_{14}$, i.e. free of actinides and containing 1 atom $Me^{2+} + Me^{3+}$ per 14 O. The composition variables in Eq. 1 are as follows:

$X_{Me3+} = Me^{3+}/(Me^{2+} + Me^{3+})$; $X_{REE} = REE/(Ca + REE)$; $X_{Me5+} = Me^{5+}/(Ti + Me^{5+})$

> Note: To derive Eq. 1, compositions of three endmembers suggested in this study, $Ca_2Zr_2Me^{5+}_2TiMe^{2+}O_{14}$, $Ca_2Zr_2Ti_2Me^{5+}Me^{3+}O_{14}$, $CaREEZr_2Ti_3Me^{3+}O_{14}$, were projected as points in a 3-dimensional (X_{REE}, X_{Me5+}, X_{Me3+}) linear Cartesian space. These points were fitted by a general form of the equation of a plane $a * X_{REE} + b * X_{Me^{5+}} + c * X_{Me^{3+}} + d = 0$ to determine coefficients *a, b, c, d* which are $\frac{2}{3}, 1, \frac{1}{3}, -\frac{2}{3}$.

For actinide-bearing zirconolite and zirconolite containing ≤ 1 $Me^{2+} + Me^{3+}$ atom per 14 O, i.e. compositions expressed as $(Ca,REE,ACT)_2Zr_2(Ti,Me^{5+})_3(Me^{2+},Me^{3+},Ti)O_{14}$, the calculation is modified to consider participation of ideal zirconolite, $Ca_2Zr_2Ti_4O_{14}$, and $CaACTZr_2Ti_3Me^{2+}O_{14}$. The fraction of the former is subtracted from other endmembers (the variable X_{id} is a fraction of uncoupled ideal zirconolite in the solid solution), while the latter is projected at the same point as $REE_2Zr_2Ti_3Me^{2+}O_{14}$ in Fig. 11. For this extended system, the calculation is as follows:

$X_{Me3+} = 2-2X_{REE*}-3X_{Me5+*}$ (2)

The modified variables are expressed as follows:

$$X_{REE*} = \frac{(REE+2ACT)}{[REE+ACT+Ca-2X_{id}]}   (3)$$

$$X_{Me5+*} = \frac{Me^{5+}}{[Me^{5+}+Ti-4X_{id}]}   (4)$$

$$X_{id} = \frac{4(Ti+Me^{5+})}{(Me^{2+}+Me^{3+}+Me^{5+}+Ti)} - 3   (5)$$