Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for publication

An investigation of the interactions of Eu^{3+} and Am^{3+} with uranyl minerals: implications for the storage of spent nuclear fuel

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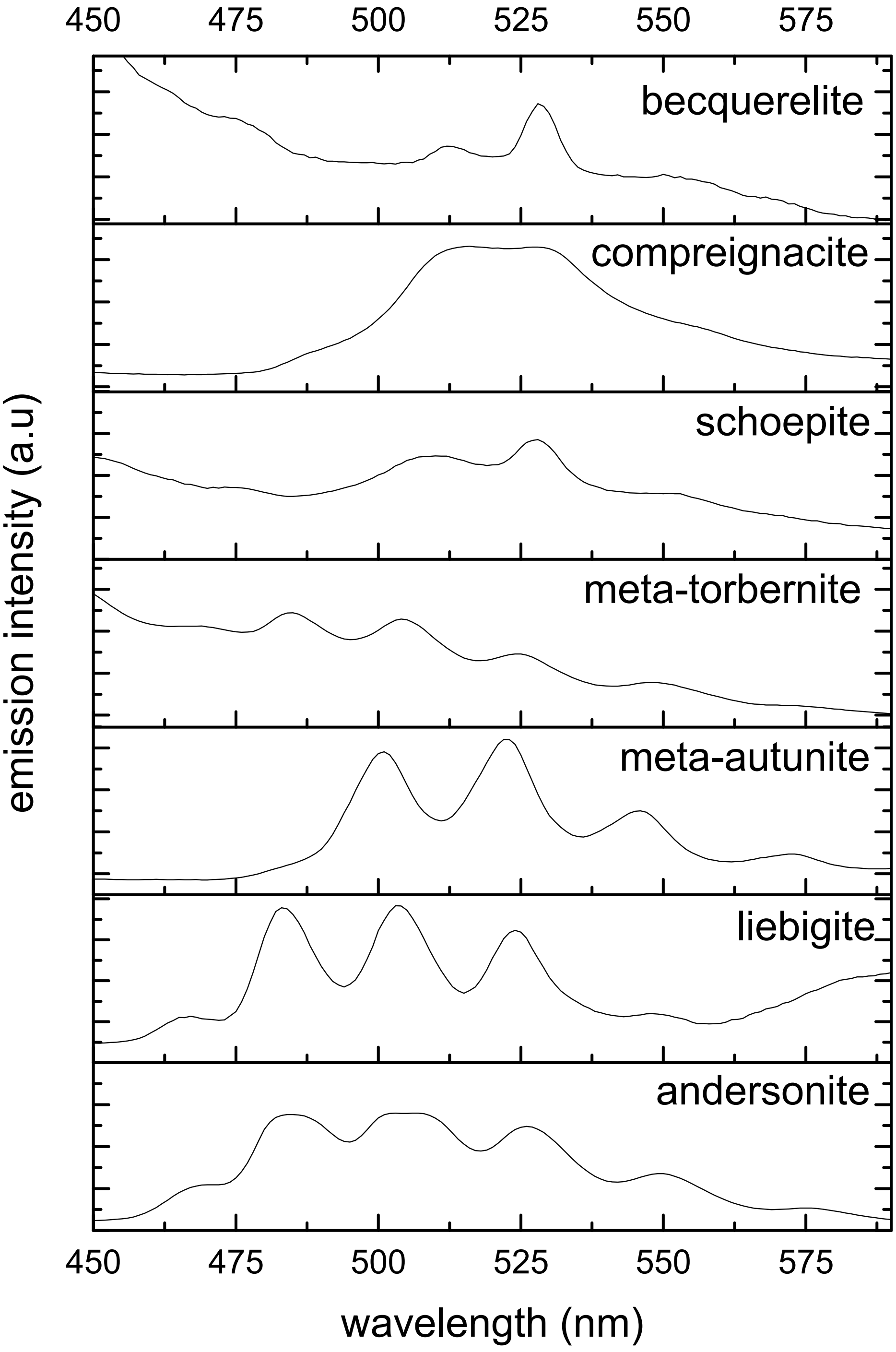


Figure S1. Emission spectra of uranyl minerals used in this study (λ_{ex} = 340 nm, T= 300 K). Spectra are identical to that reported in the literature (becquerelite;[1] compreignacite[2]; schoepite[3]; meta-torbernite[3]; meta-autunite[3]; liebigite[3] andersonite[4]). Cuprosklodowskite is non-emissive at room temperature consistent with the literature.[5]

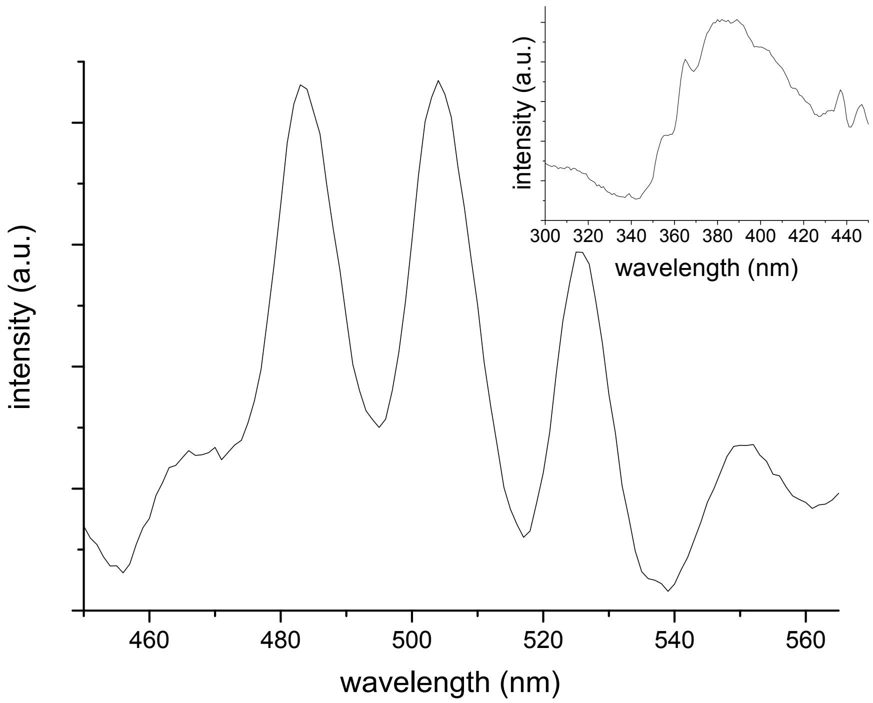


Figure S2. Uranyl emission spectrum of grimselite (λ_{ex} = 380 nm; T = 300 K). Insert shows the excitation spectrum (λ_{em} = 503 nm).

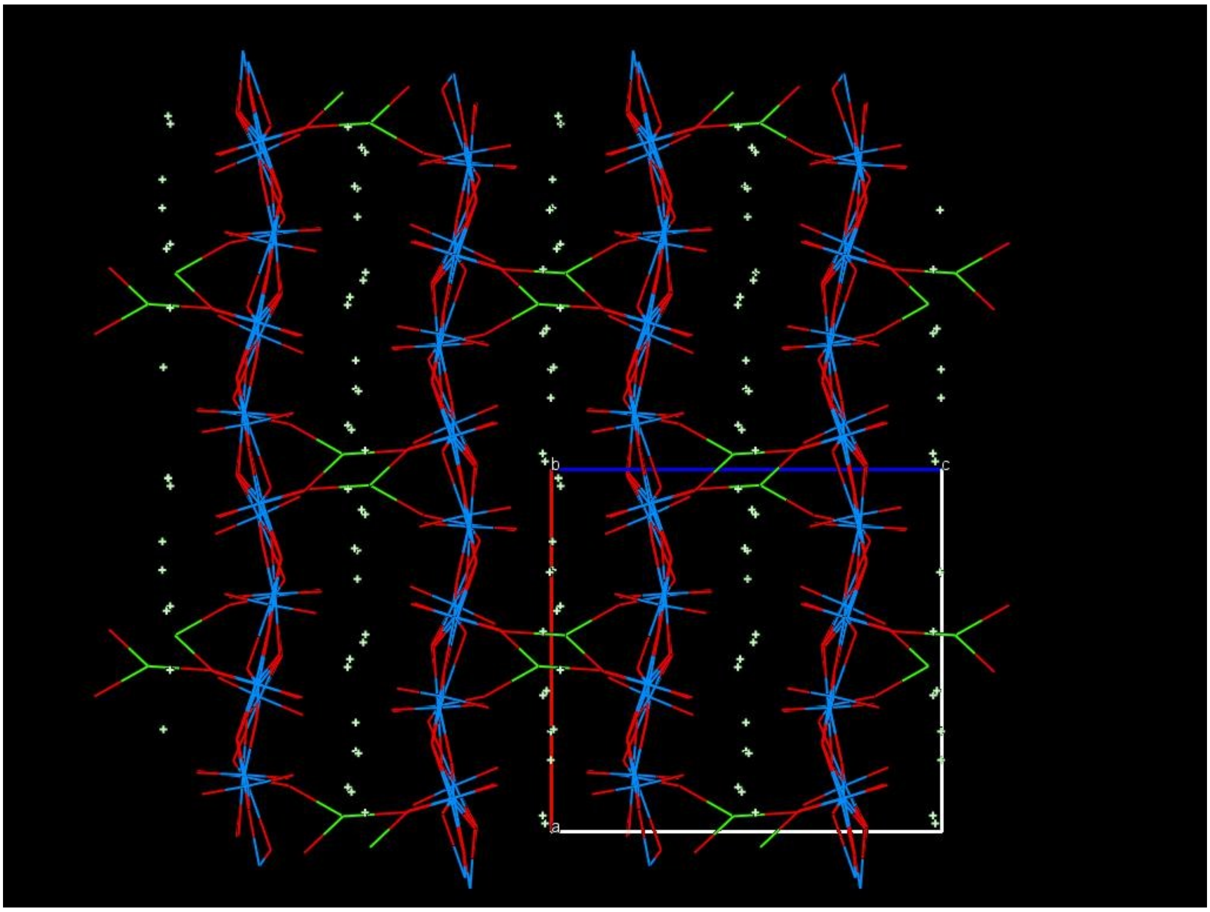


Figure S3. Solid state structure of becquerelite along the crystallographic *b* axis from Ref [6]. Colour code – U = blue, O = red, Ca = green.

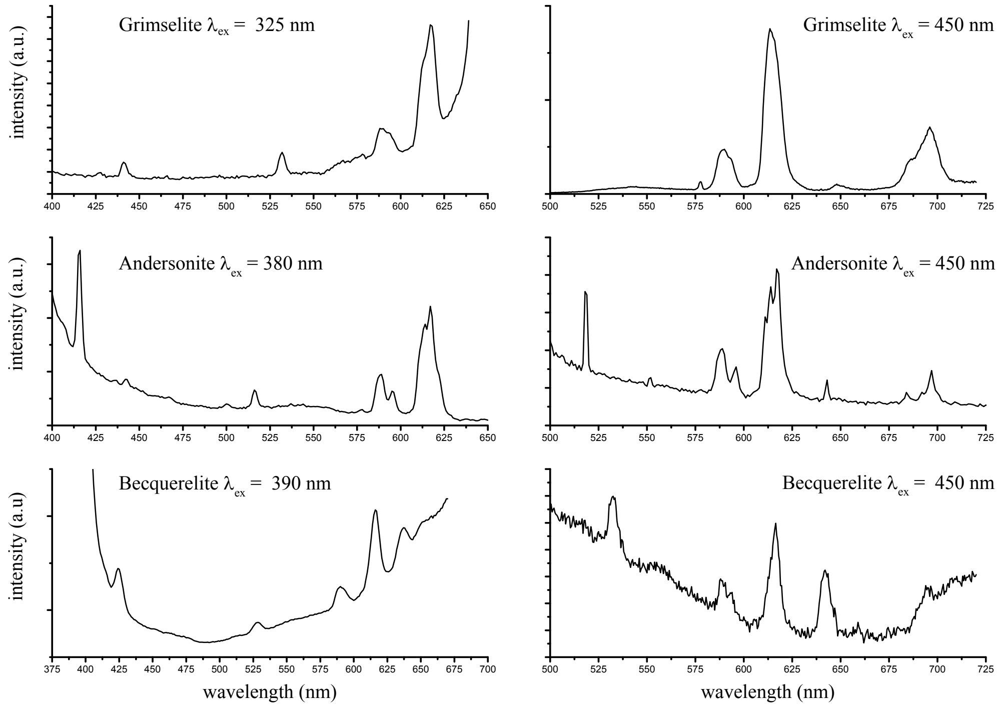


Figure S4. Solid-state emission spectra of the Eu containing minerals displaying the uranyl region at two different excitation wavelengths.

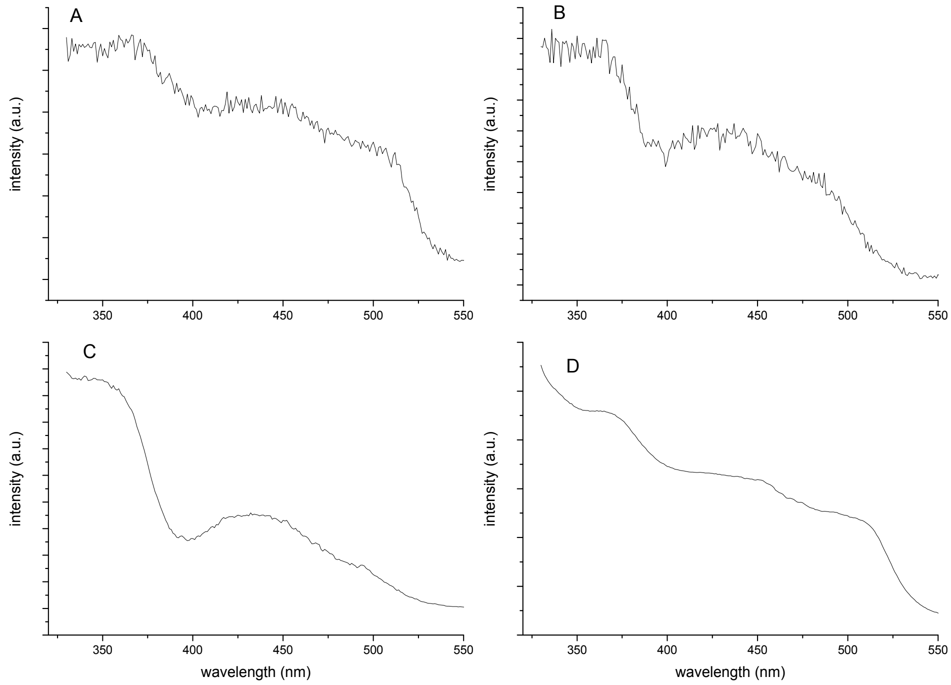


Figure S5. Excitation spectra of Eu containing minerals (λ_{em} = 615 nm): (a) becquerelite; (b) leigbigite; (c) andersonite; (d) grimselite.

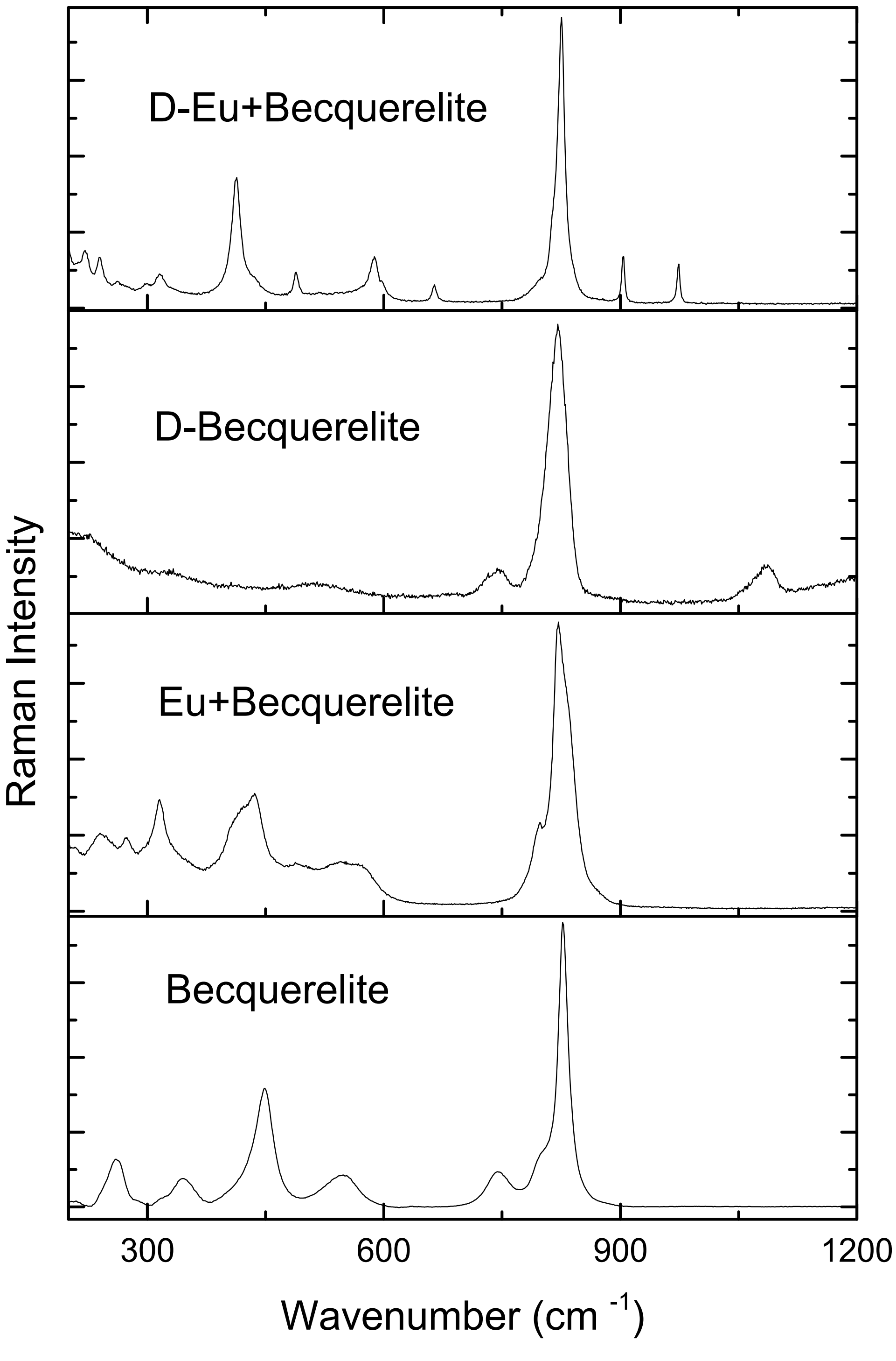


Figure S6. Raman Spectra of becquerelite and Eu incorporated becquerelite.

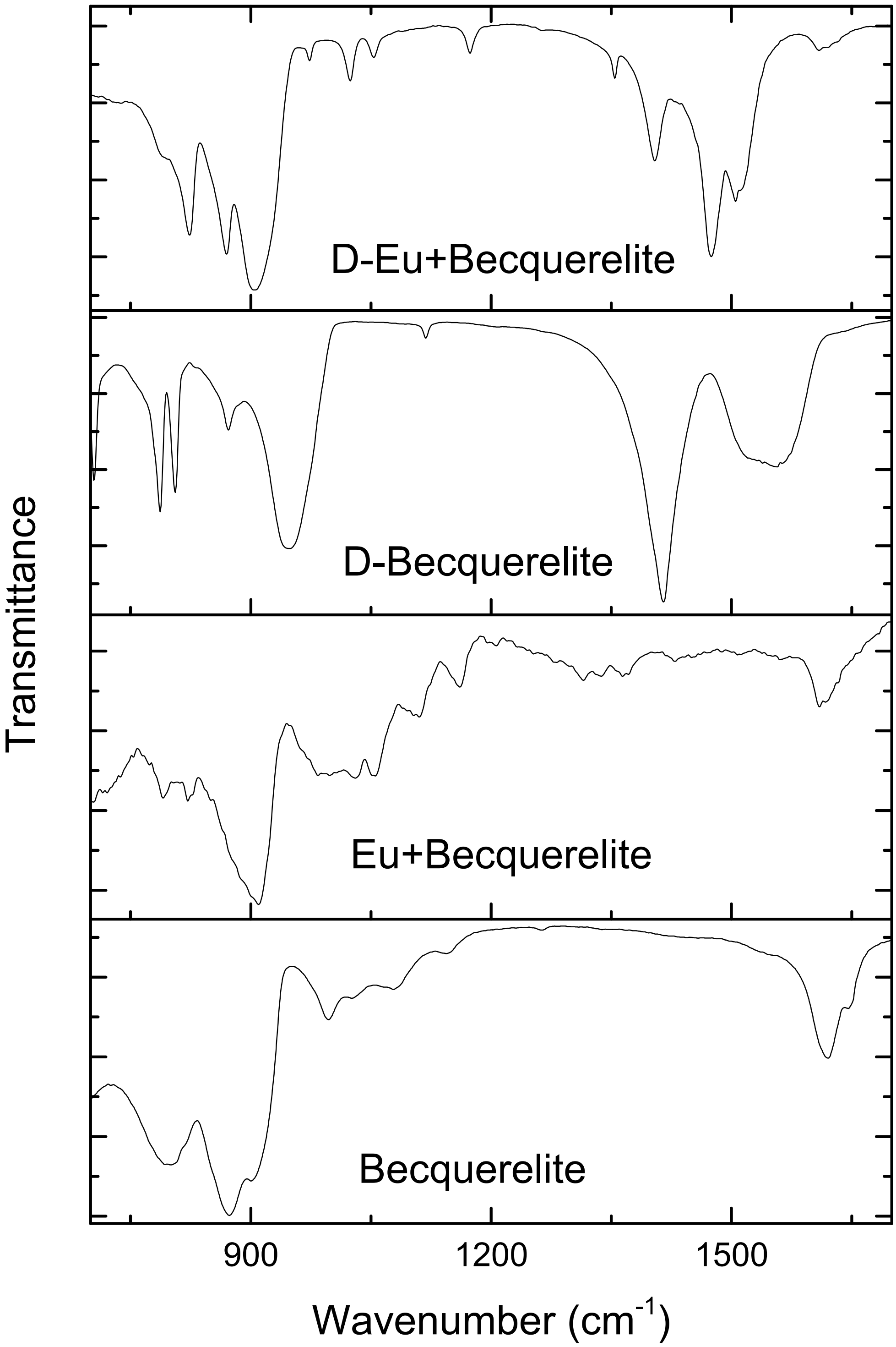
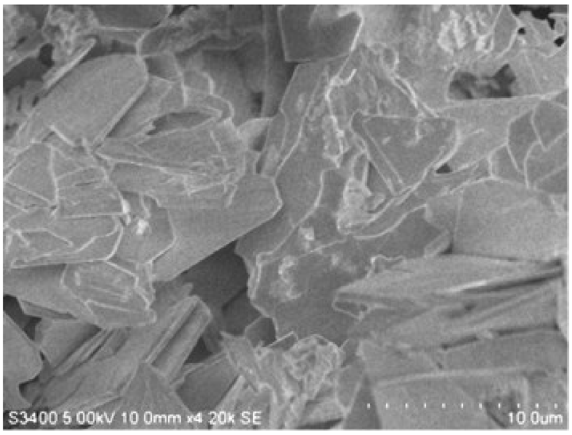


Figure S7. IR Spectra of becquerelite and Eu incorporated becquerelite.



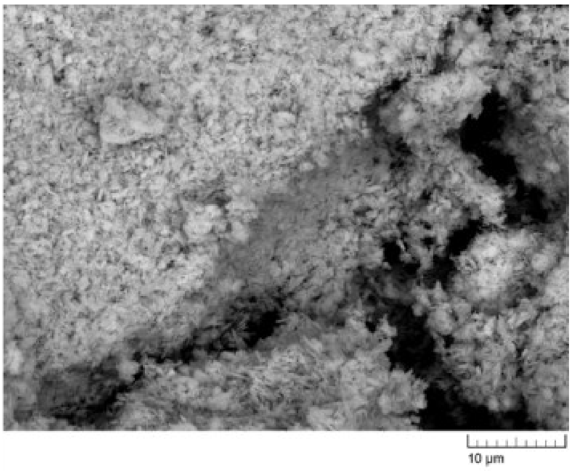


Figure S8. SEM images of becquerelite (left) and Eu^{3+} incorporated becquerelite (right). Scale bar = 10 μm.

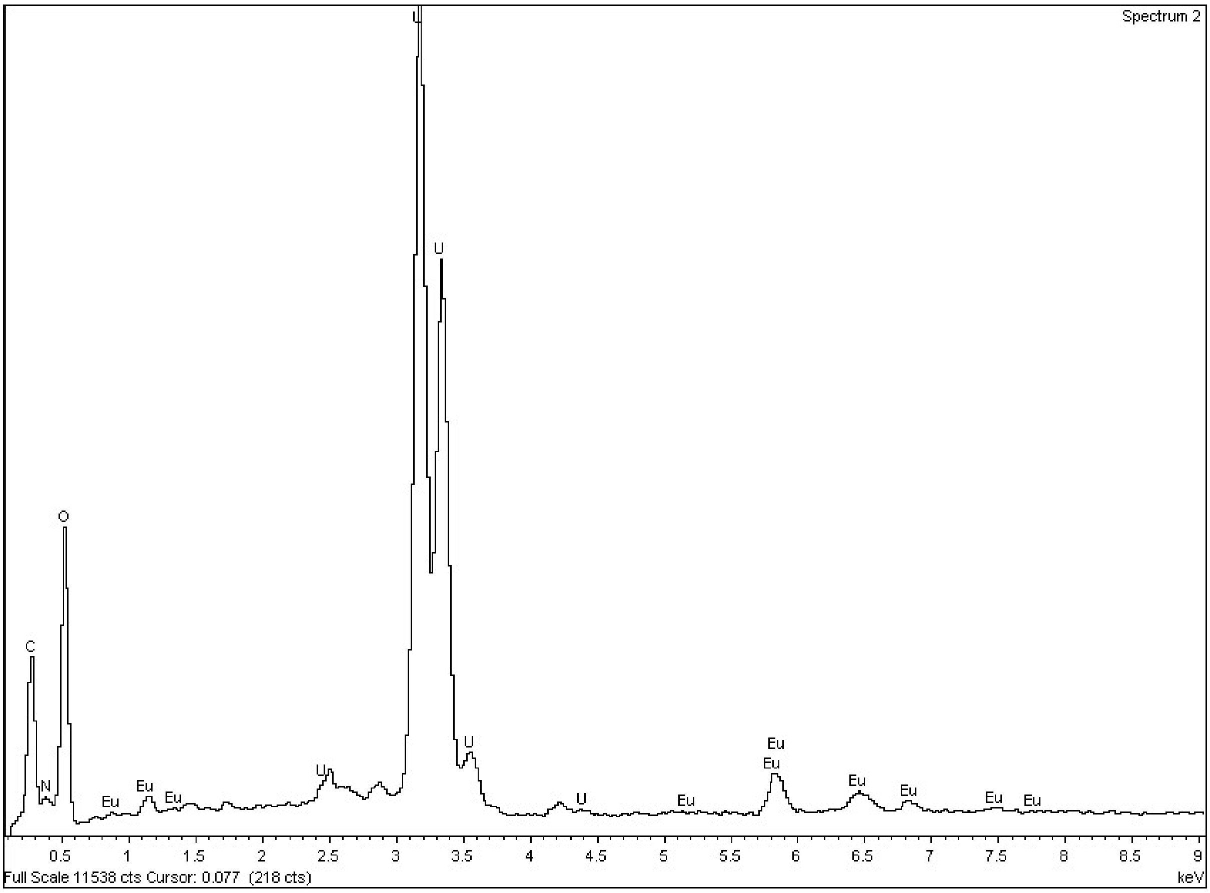


Figure S9. EDX measurements for Eu incorporated becquerelite (C signal arises from the carbon coating treatment).

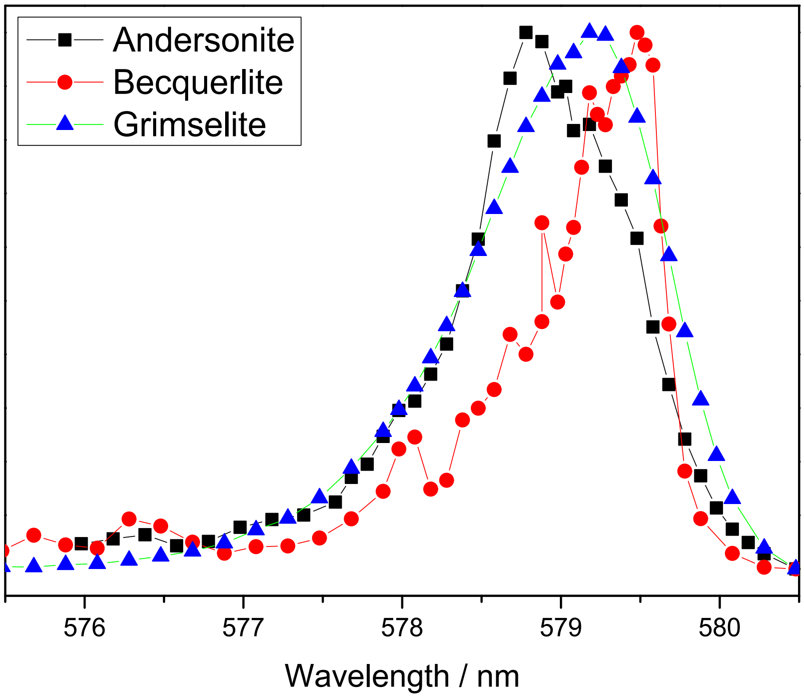


Figure S10. Low temperature excitation spectra of grimselite, andersonite and becquerelite (λ_{em} = $\sum_{Intensity}$ 605 – 630 nm).

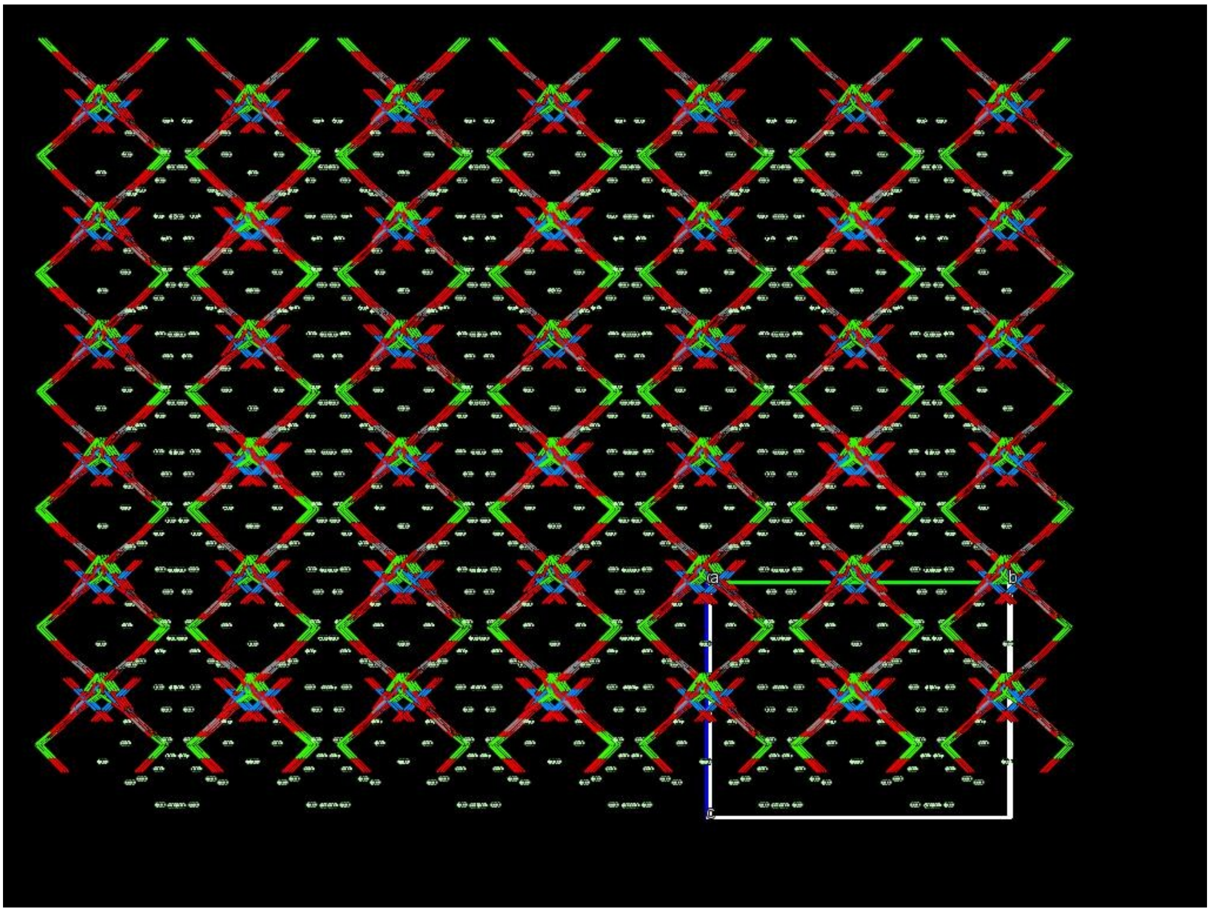


Figure S11. Solid state structure of liebigite along the crystallographic *a* axis, taken from Ref [7]. Colour code – U = blue, O = red, Ca = green.

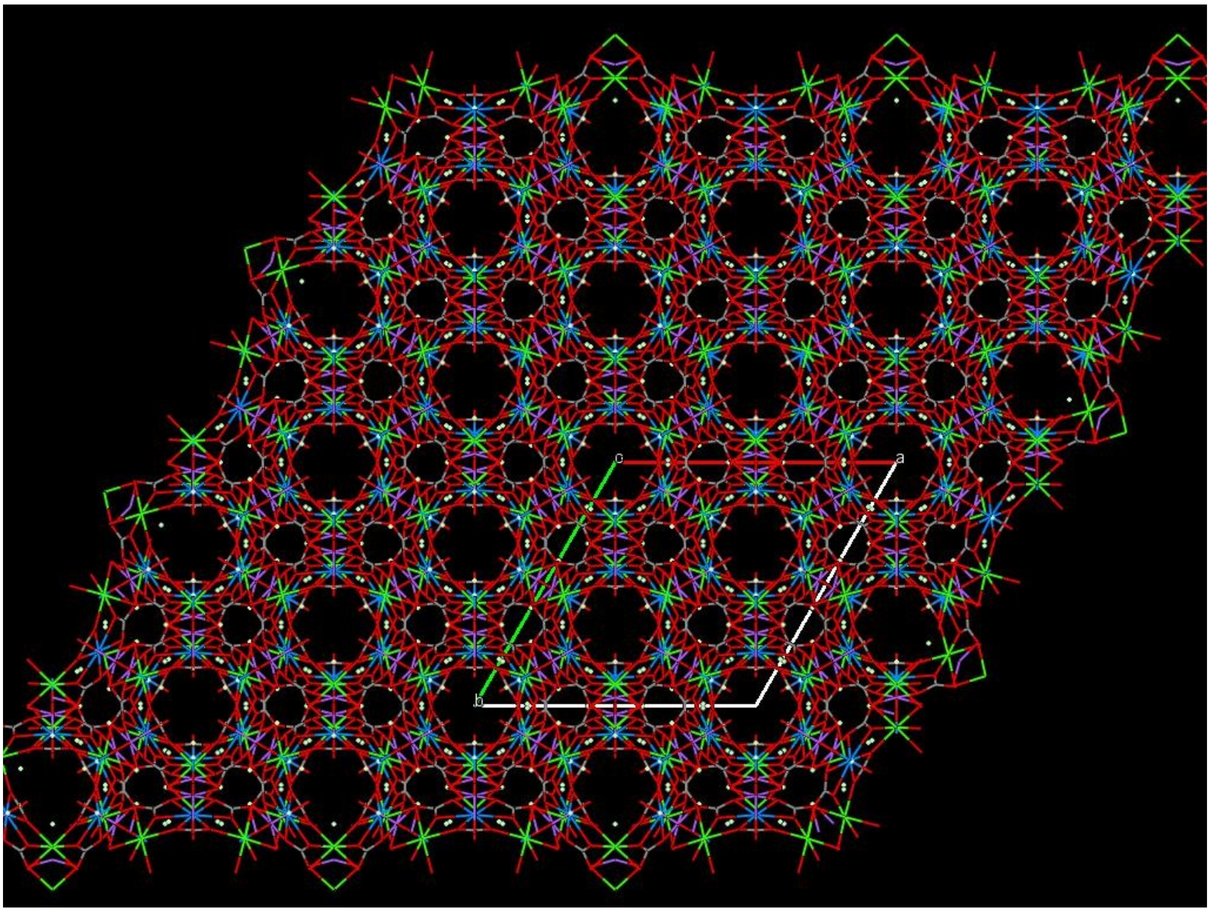


Figure S12. Solid state structure of andersonite along the crystallographic *c* axis, taken from Ref [8]. Colour code – U = blue, O = red, Ca = green, Na = purple.

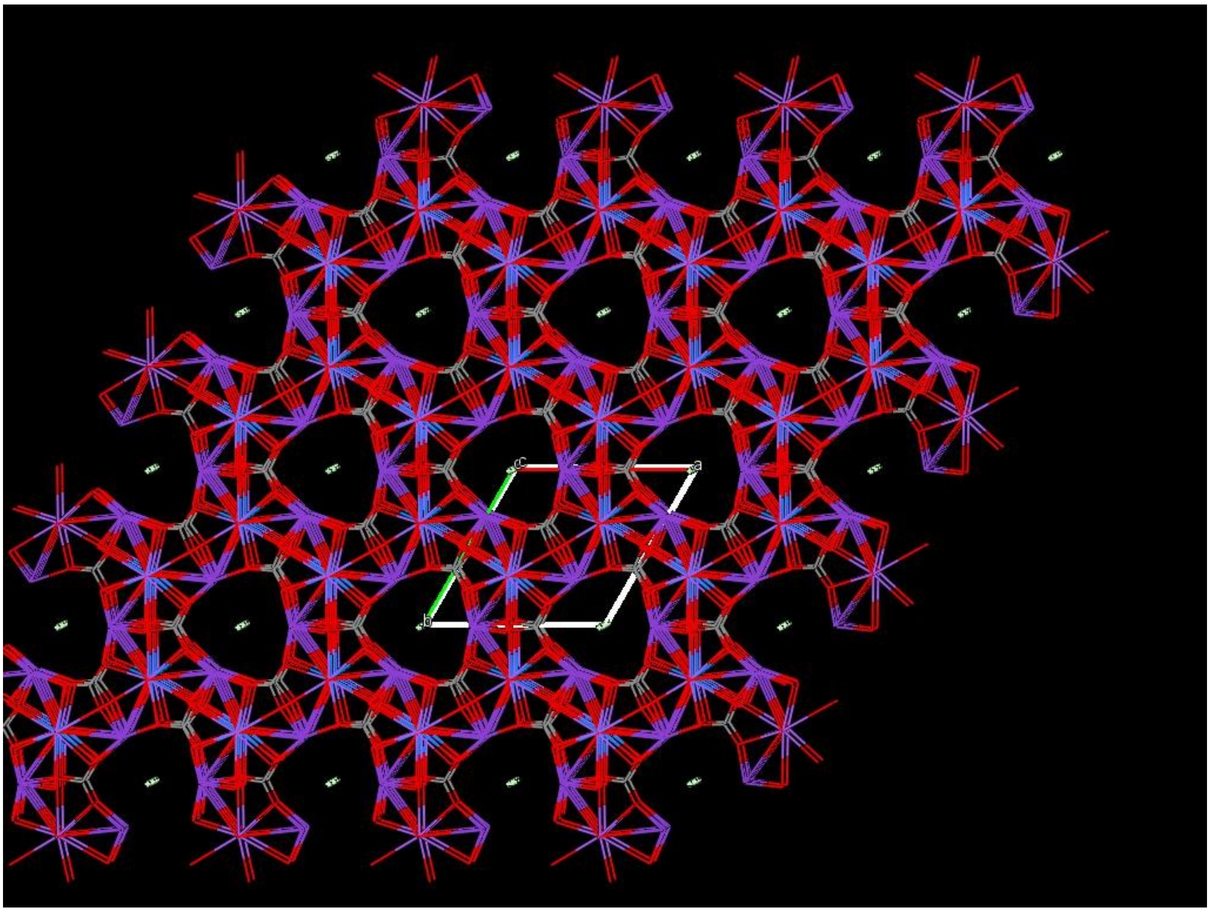


Figure S13. Solid state structure of Grimselite along the crystallographic *c* axis, taken from Ref [9].

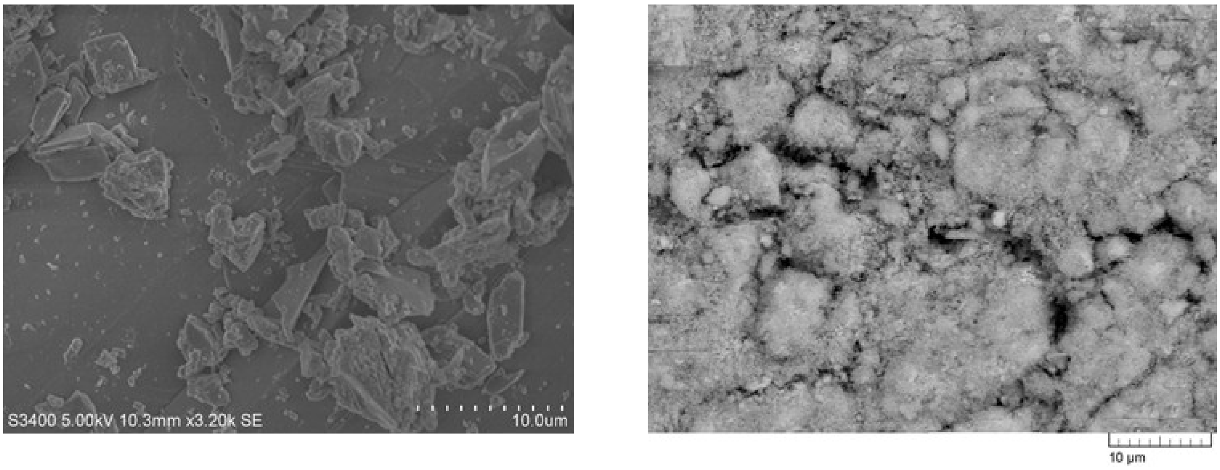


Figure S14. SEM images of andersonite (left) and Eu^{3+} incorporated andersonite (right). Scale bar = 10 μm.

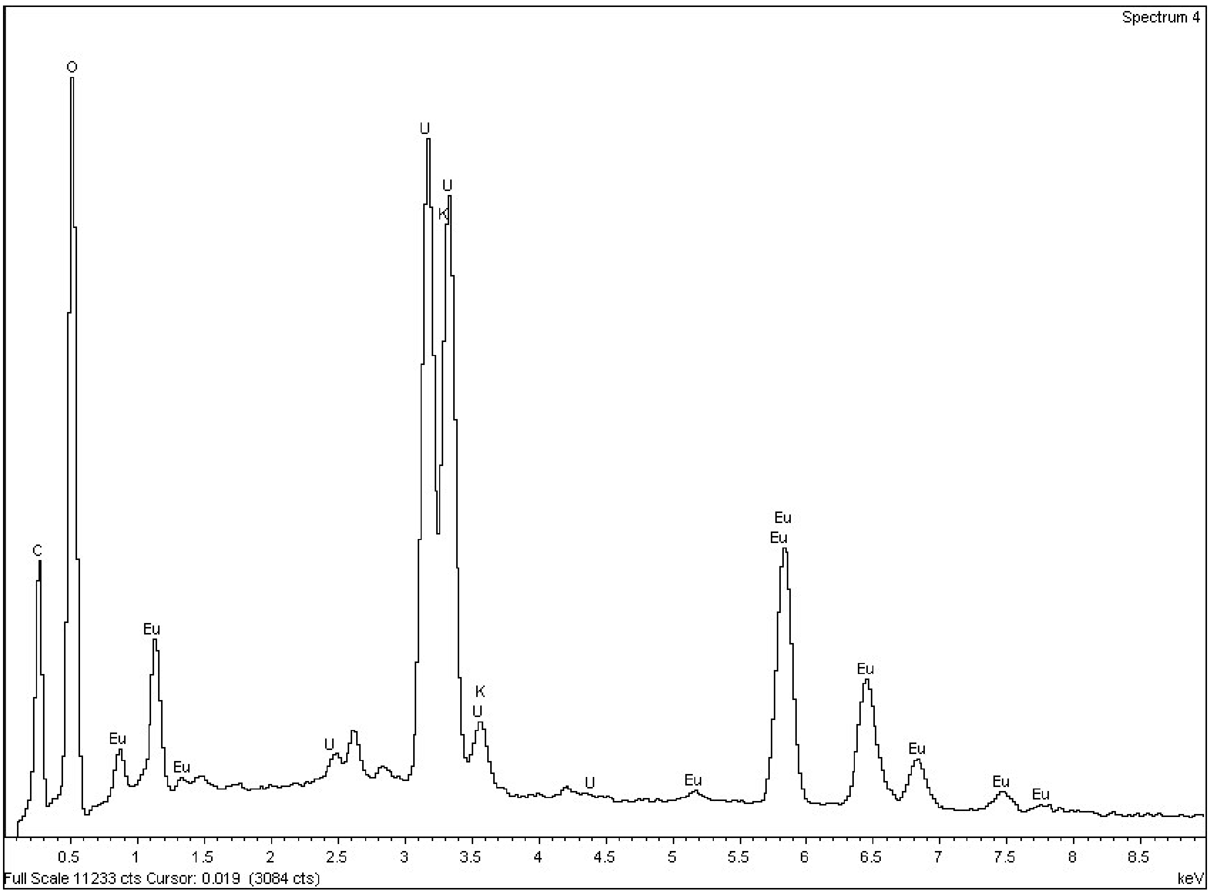


Figure S15. EDX measurements for Eu Incorporated andersonite.

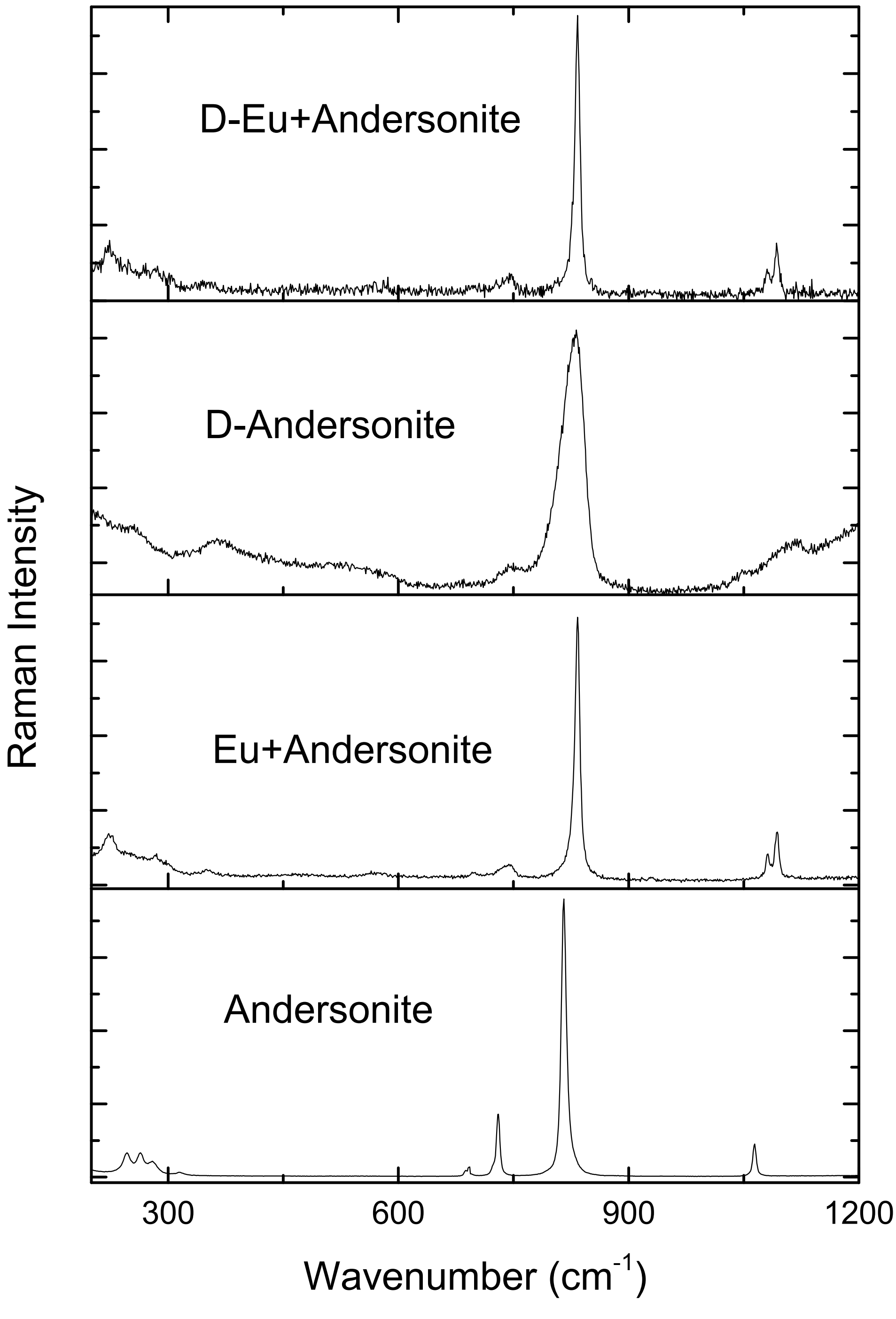


Figure S16. Raman Spectra of andersonite and Eu incorporated andersonite.

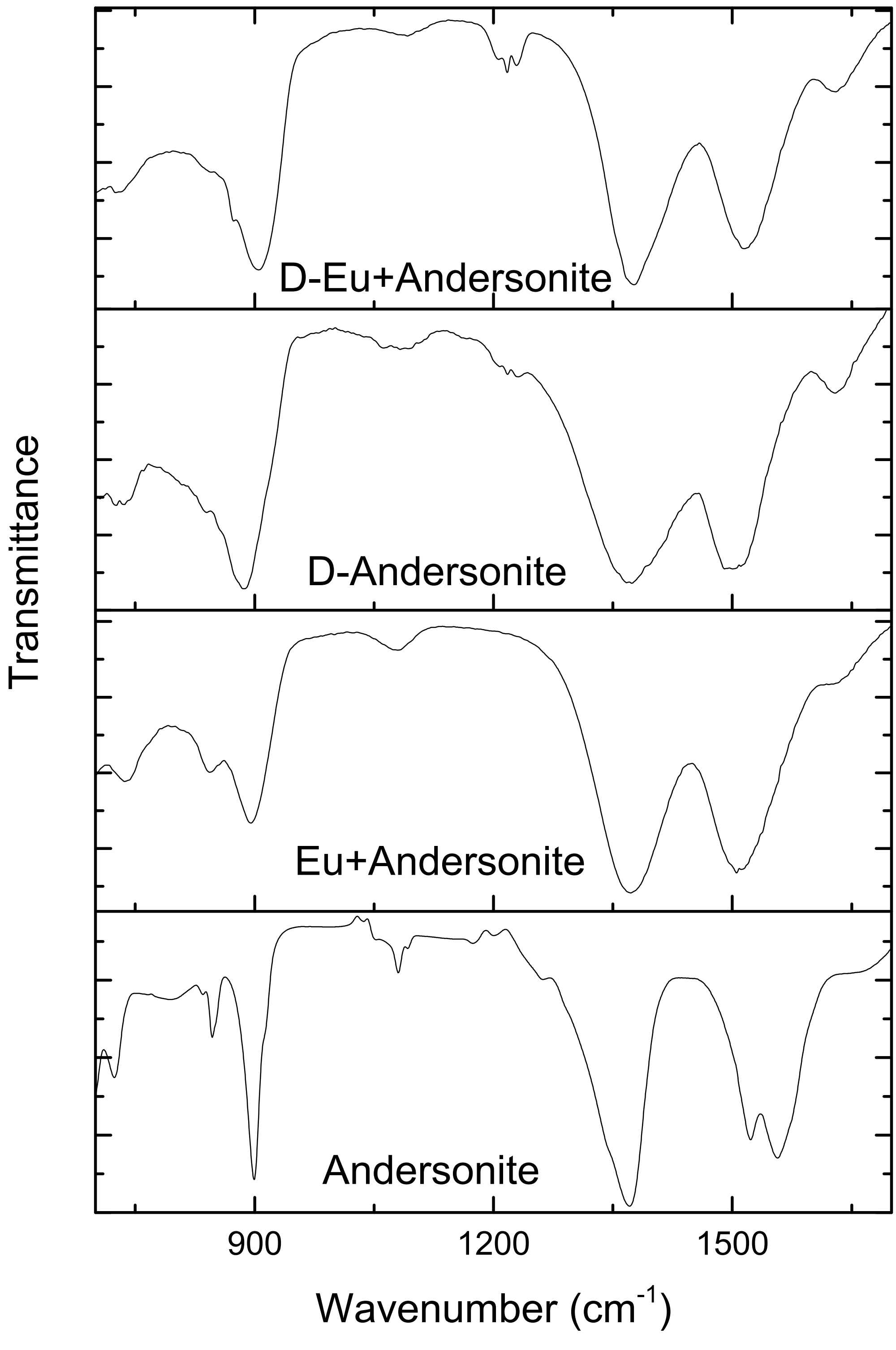
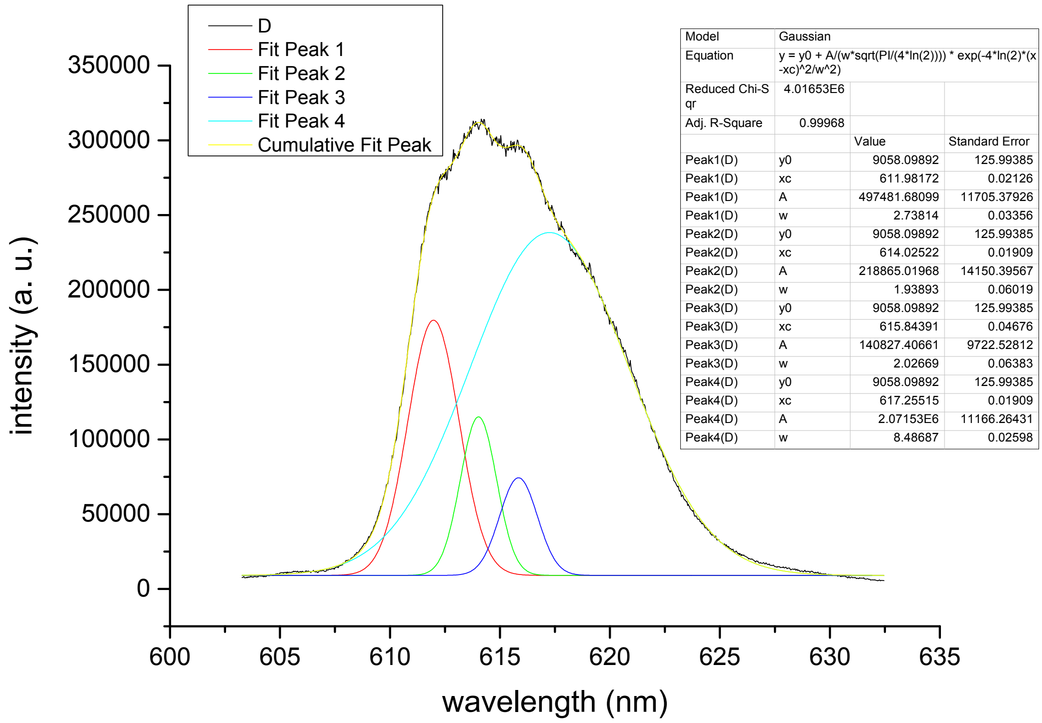
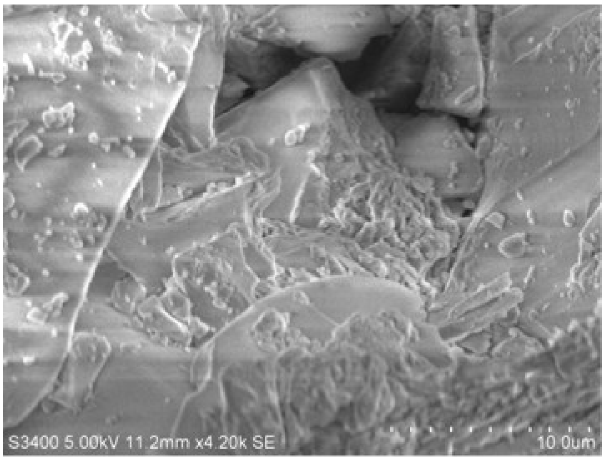


Figure S17. IR Spectra of andersonite and Eu incorporated andersonite.



Model	Gaussian		
Equation	y = y0 + A/(w*sqrt(PI/(4*ln(2)))) * exp(-4*ln(2)*(x-xc)^2/w^2)		
Reduced Chi-Sqr	4.01653E6		
Adj. R-Square	0.99968		
		Value	Standard Error
Peak1(D)	y0	9058.09892	125.99385
Peak1(D)	xc	611.98172	0.02126
Peak1(D)	A	497481.68099	11705.37926
Peak1(D)	w	2.73814	0.03356
Peak2(D)	y0	9058.09892	125.99385
Peak2(D)	xc	614.02522	0.01909
Peak2(D)	A	218865.01968	14150.39567
Peak2(D)	w	1.93893	0.06019
Peak3(D)	y0	9058.09892	125.99385
Peak3(D)	xc	615.84391	0.04676
Peak3(D)	A	140827.40661	9722.52812
Peak3(D)	w	2.02669	0.06383
Peak4(D)	y0	9058.09892	125.99385
Peak4(D)	xc	617.25515	0.01909
Peak4(D)	A	2.07153E6	11166.26431
Peak4(D)	w	8.48687	0.02598

Figure S18. Curve fitting analysis for grimselite at 10 K.



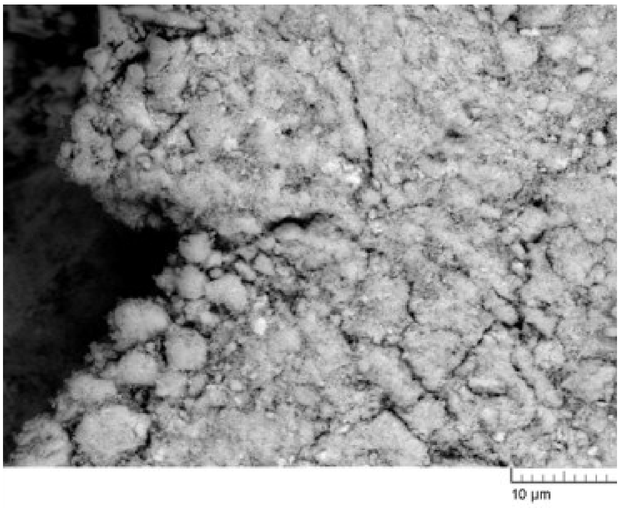


Figure S19. SEM image of grimselite (left) and Eu^{3+} contacted grimselite (right). Scale bar = 10 μm.

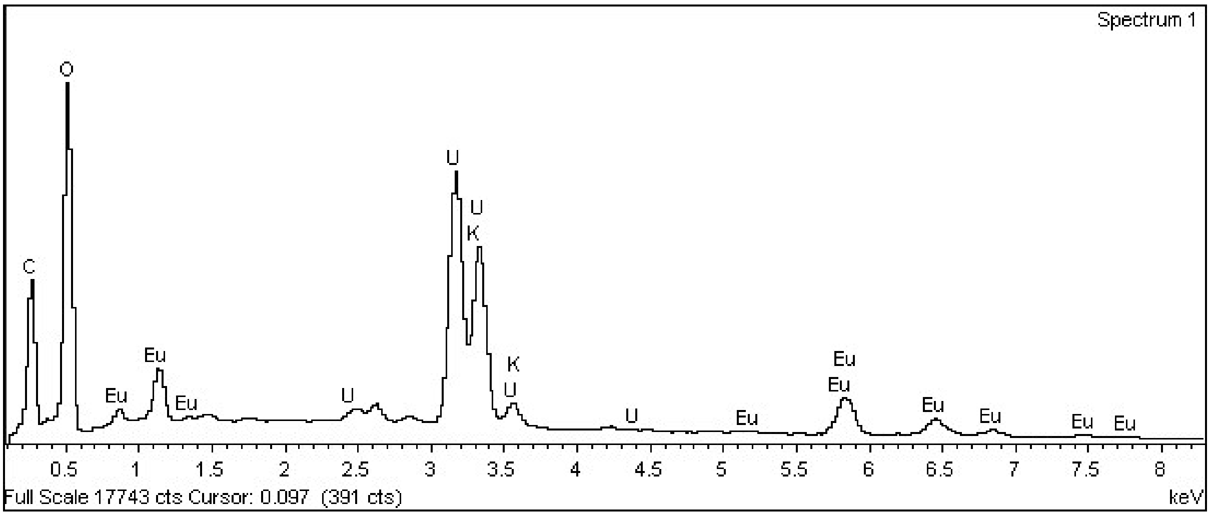


Figure S20. EDX measurements for Eu incorporated grimselite.

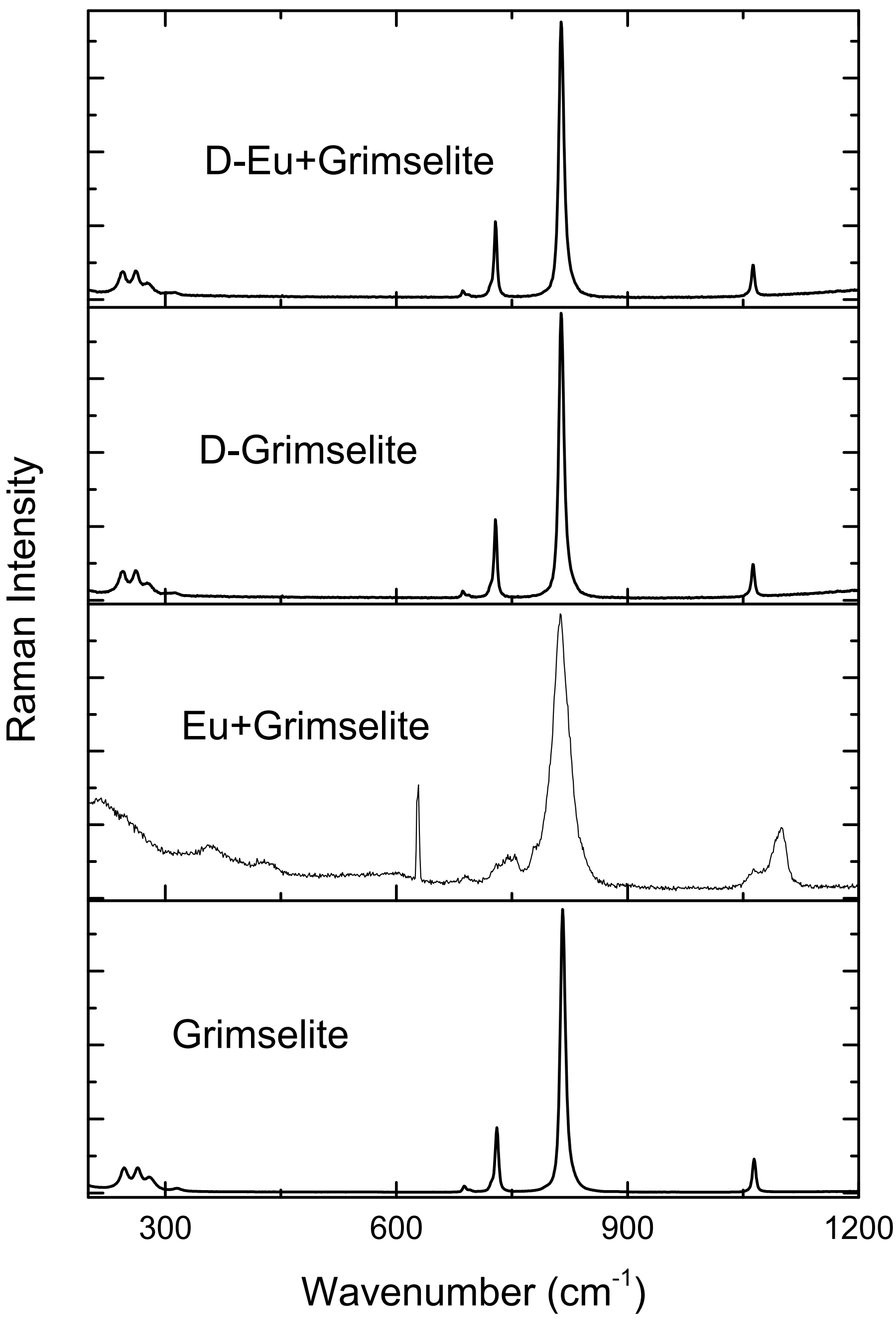


Figure S21. Raman spectra of grimselite and Eu incorporated grimselite.

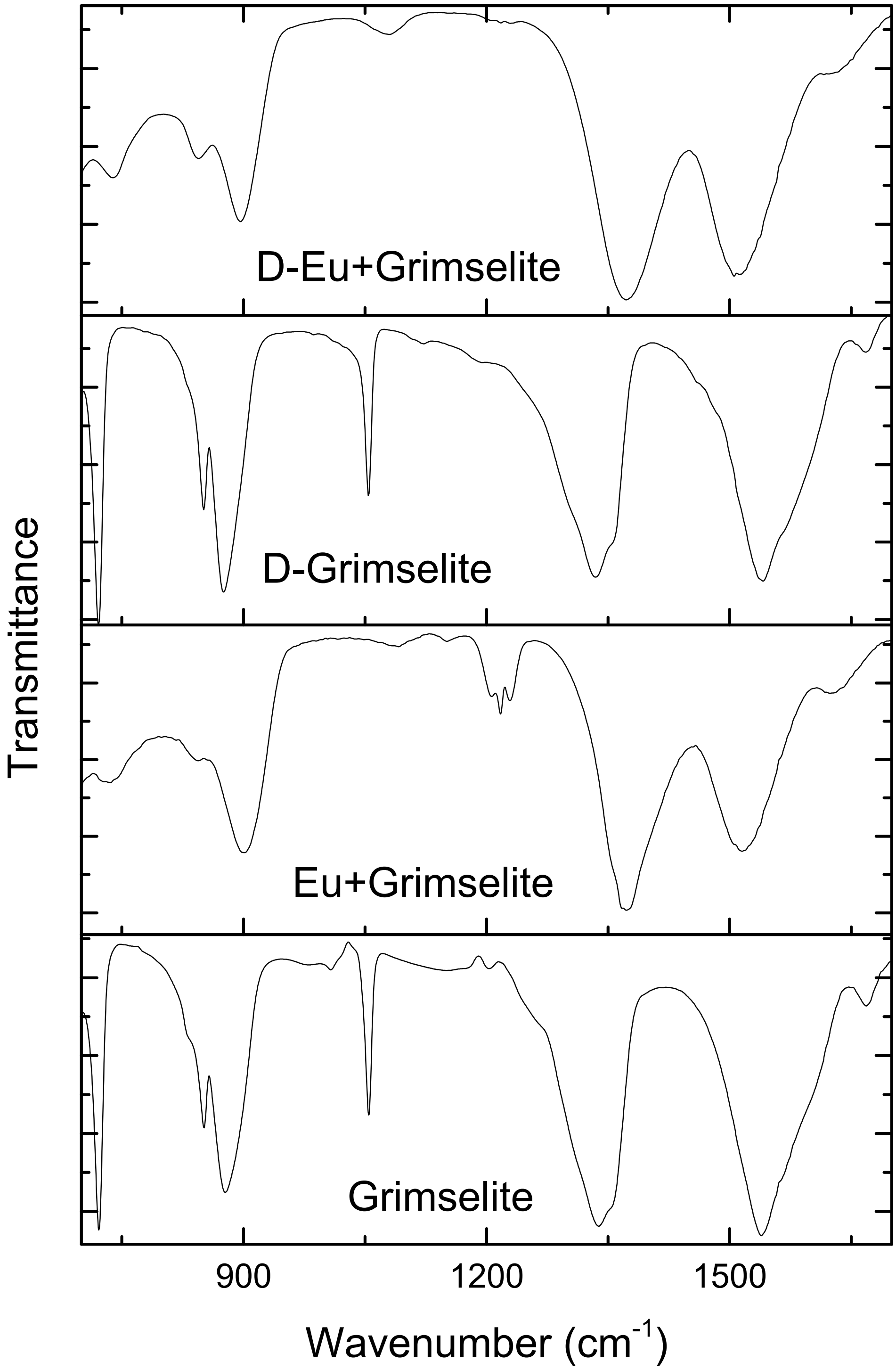


Figure S22. IR spectra of grimselite and Eu incorporated grimselite.

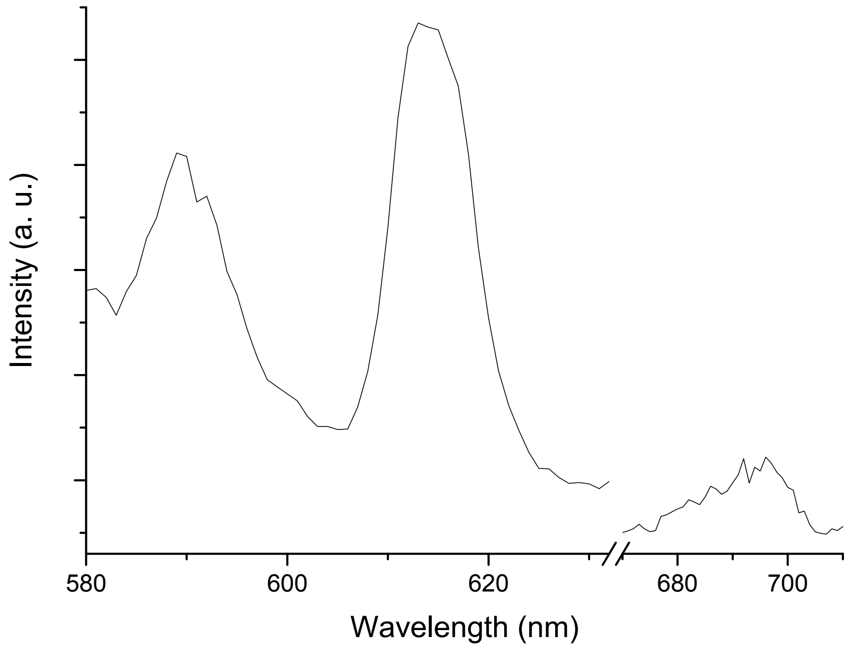


Figure S23. Solid-sate emission spectrum of Eu^{3+} incorporated liebigite at room temperature (λ_{ex} = 392 nm).

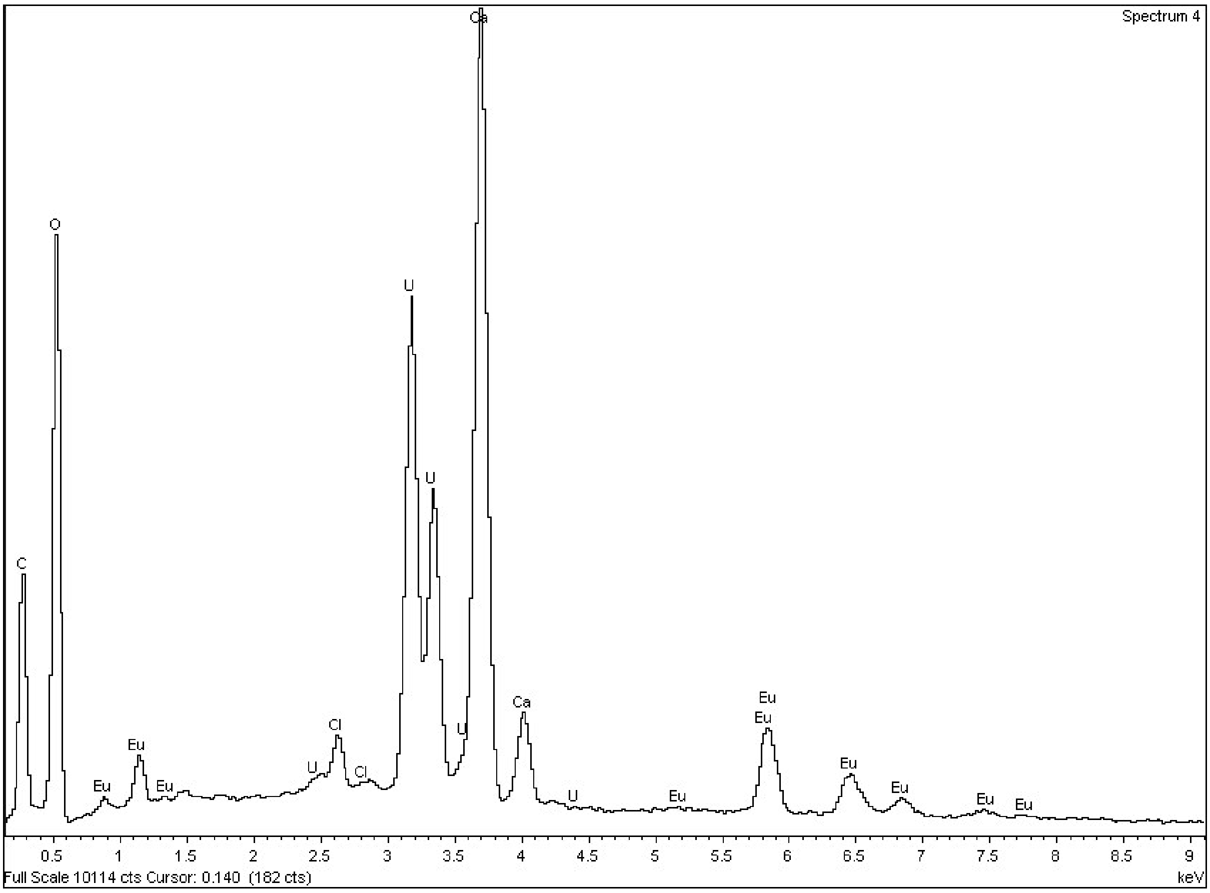


Figure S24. EDX measurements for Eu incorporated liebigite.

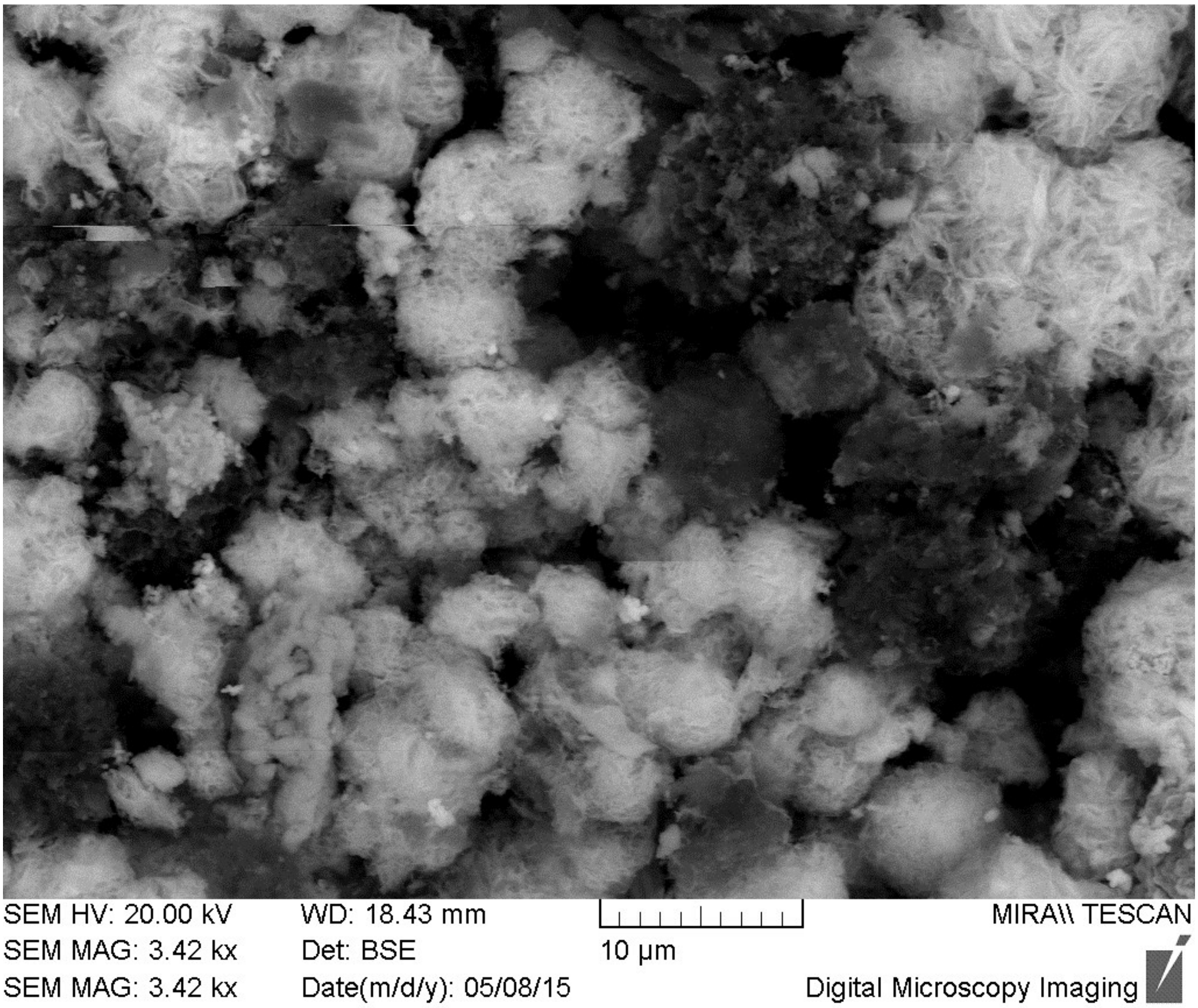


Figure S25. SEM image of Eu incorporated liebigite. Scale bar = 10 μm.

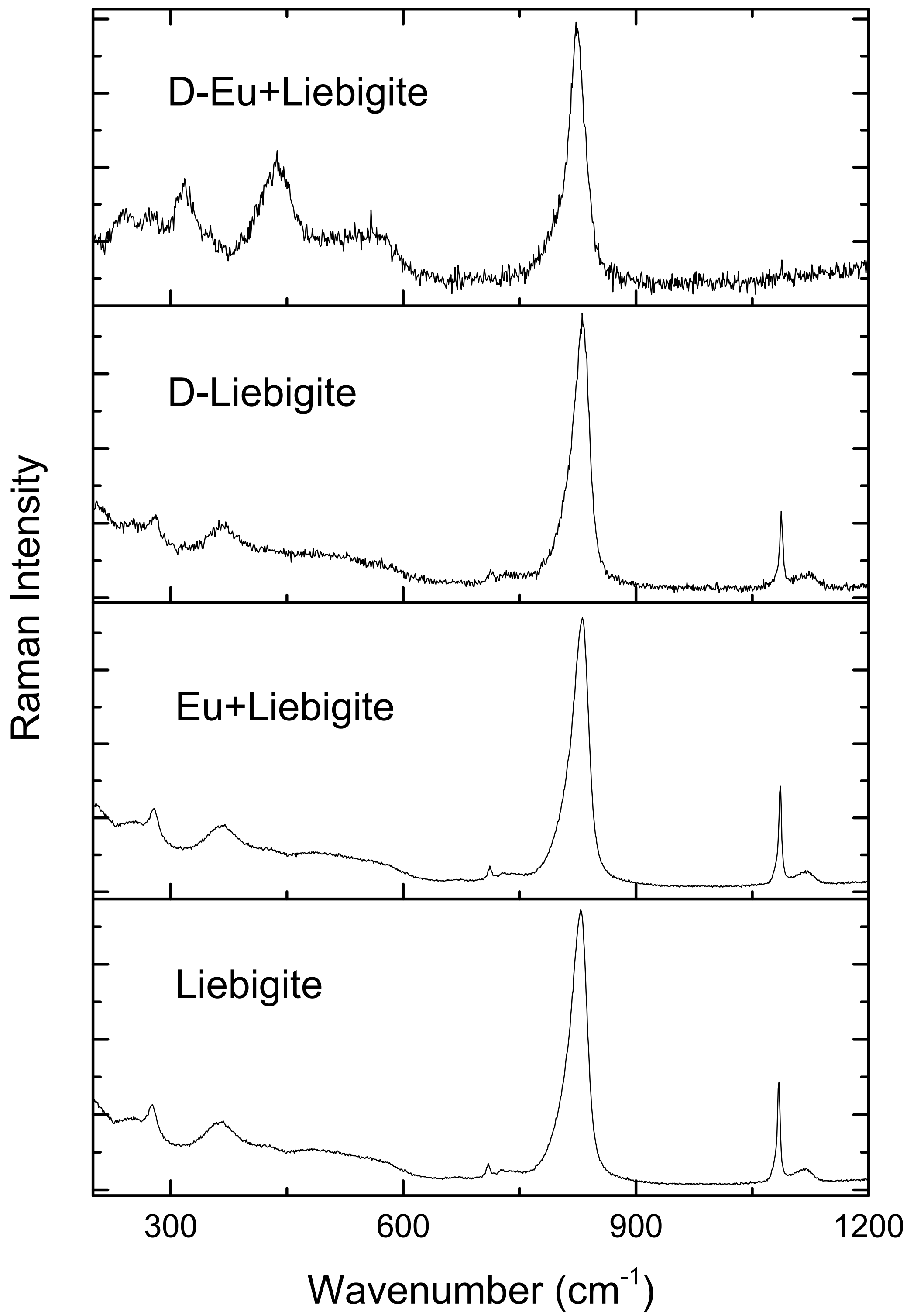


Figure S26. Raman Spectra of liebigite and Eu incorporated liebigite.

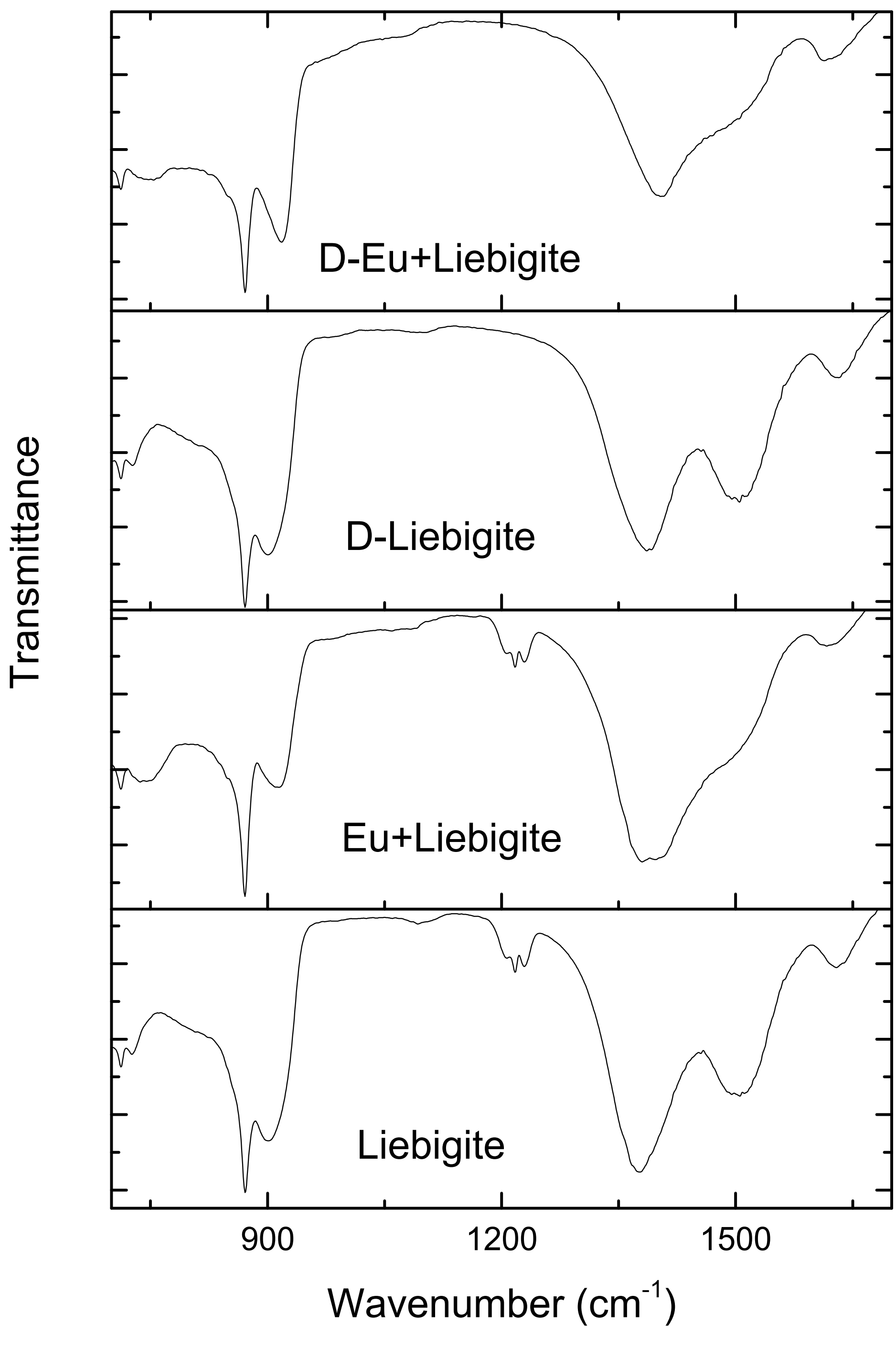


Figure S27. IR Spectra of liebigite and Eu incorporated liebigite.

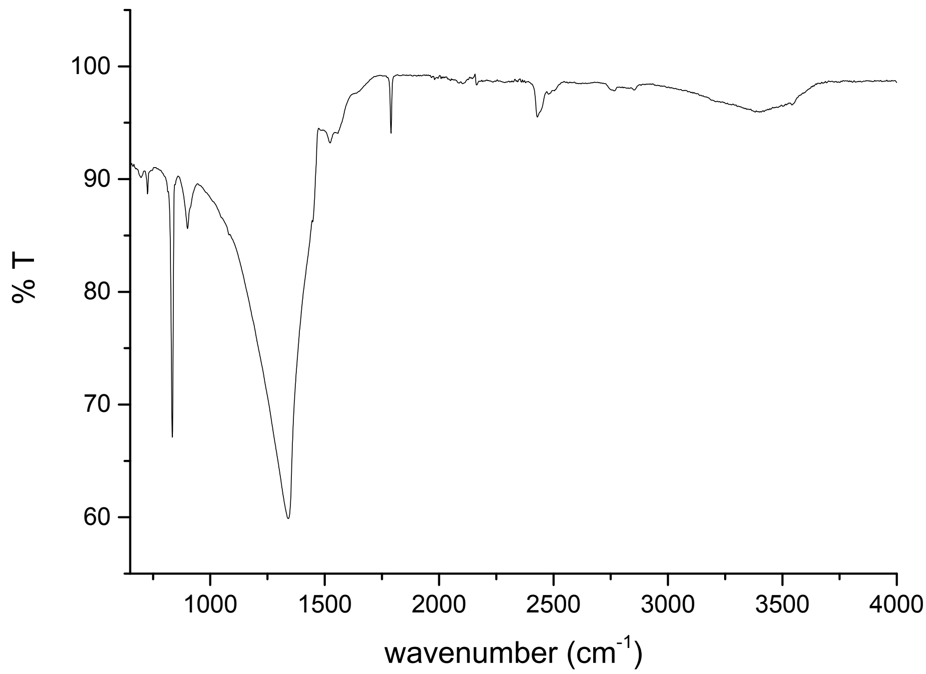


Figure S28. IR spectrum of “CaNa[UO2(NO3)3]”.

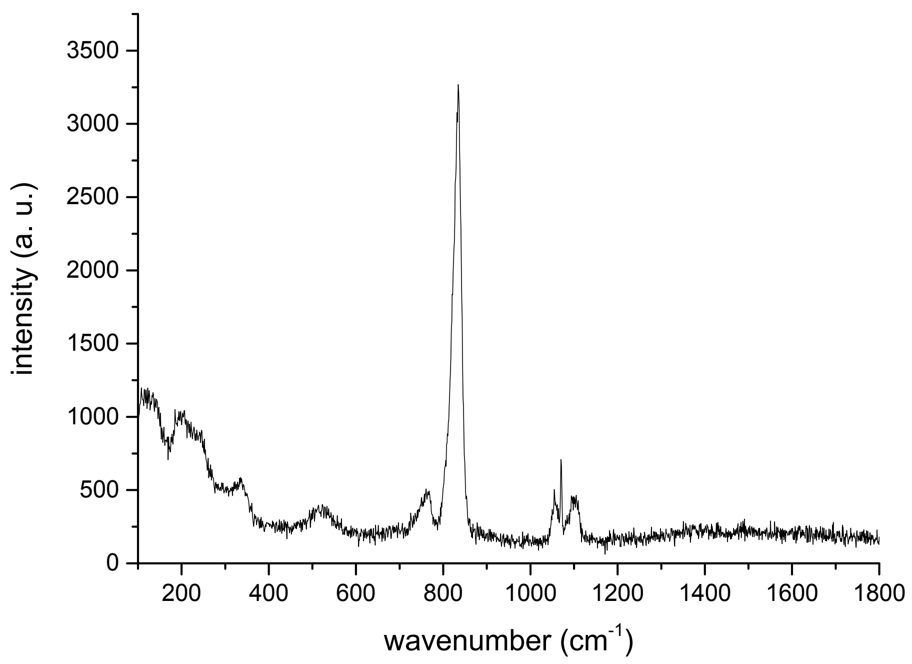


Figure S29. Raman spectrum of “CaNa[UO2(NO3)3]”.

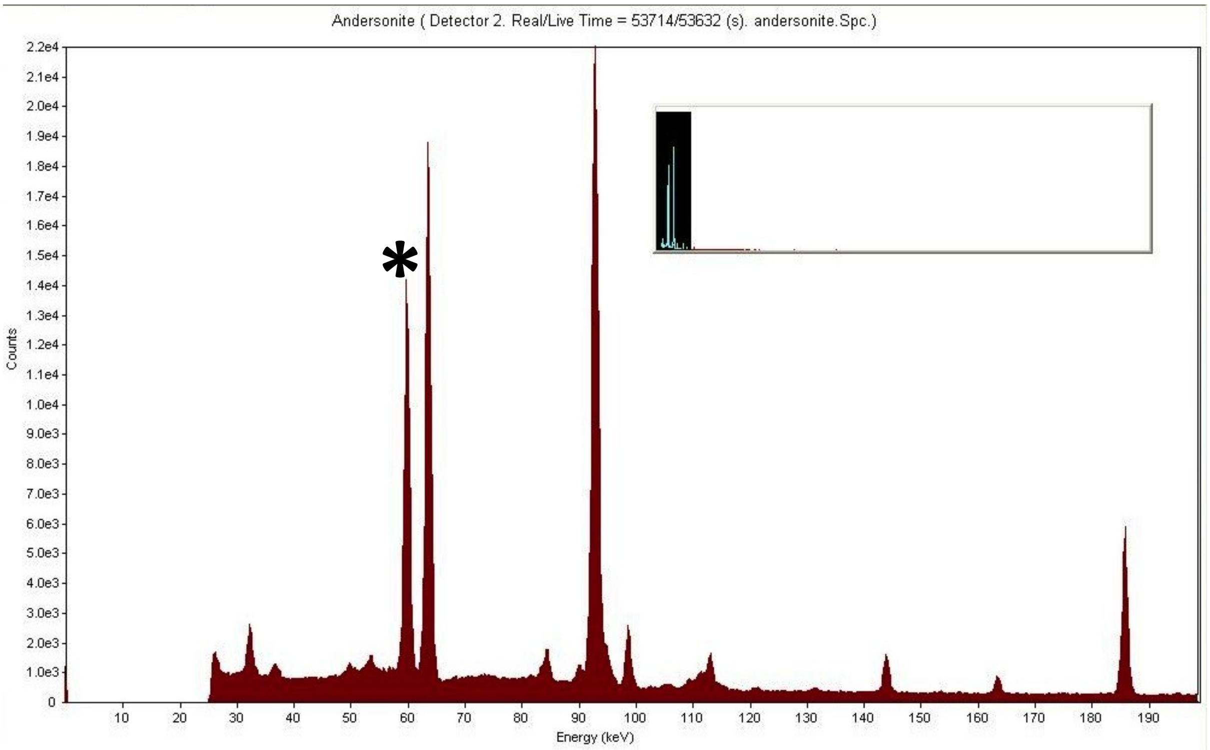


Figure S30. Typical Gamma-spectrum obtained for ^{241}Am incorporation experiments (in this case Andersonite). The peak at 59.5 keV (marked with an *) was used for the quantification of activity; the other peaks are due to uranium and its decay products.

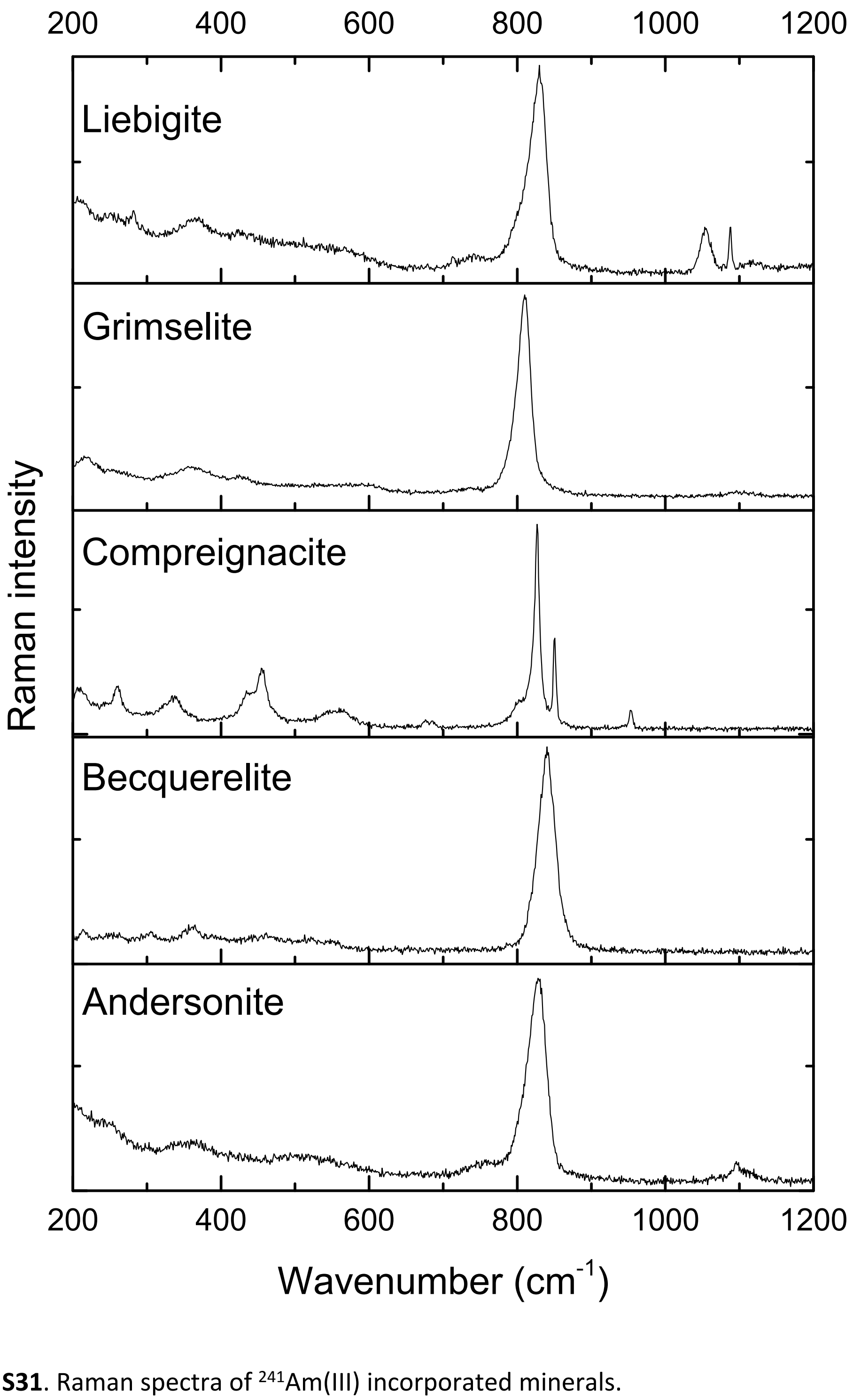


Figure S31. Raman spectra of $^{241}Am(III)$ incorporated minerals.

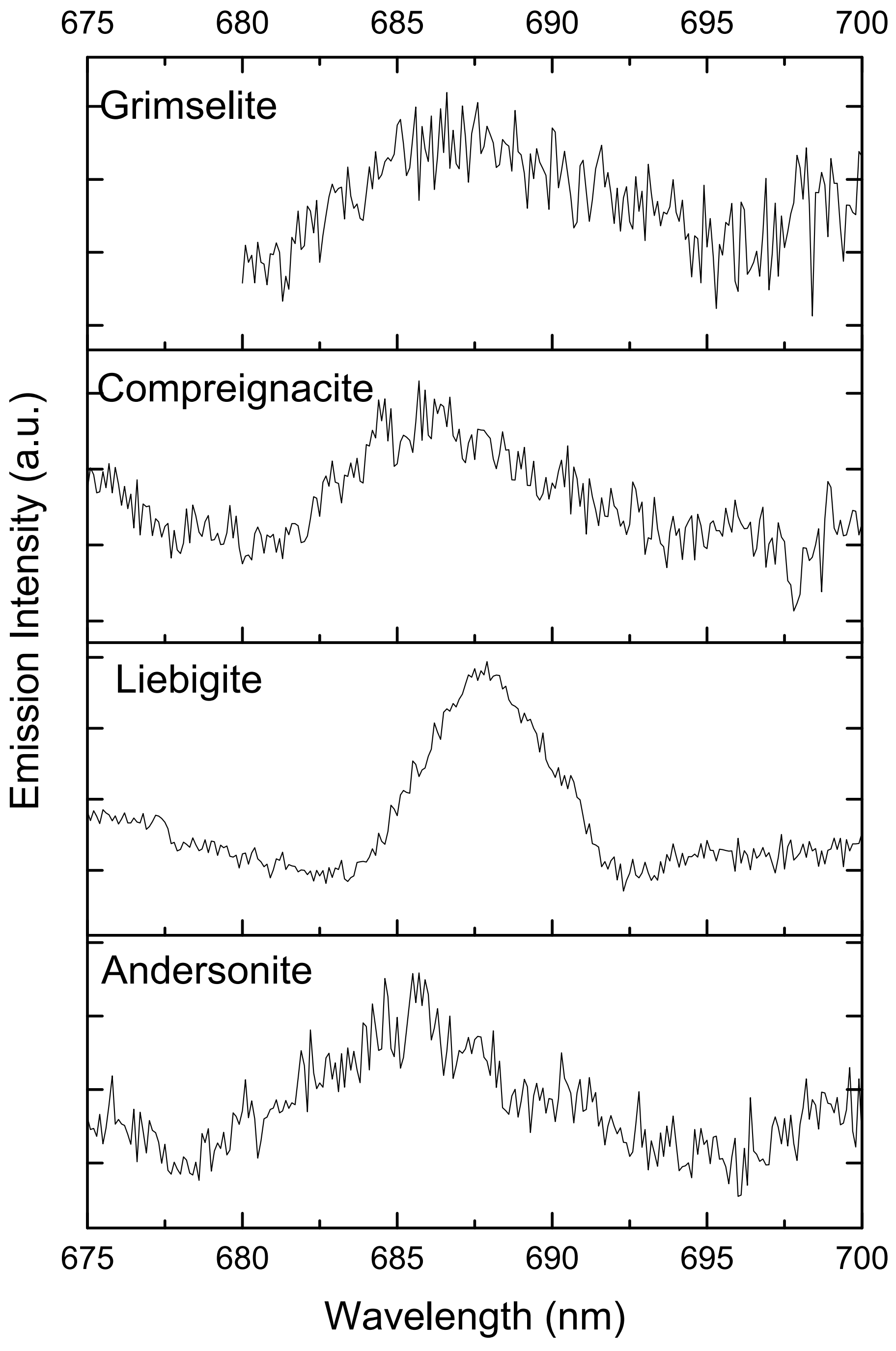


Figure S32. Solid-sate emission spectrum of $^{241}Am^{3+}$ incorporated minerals at room temperature (λ_{ex} = 504 nm).

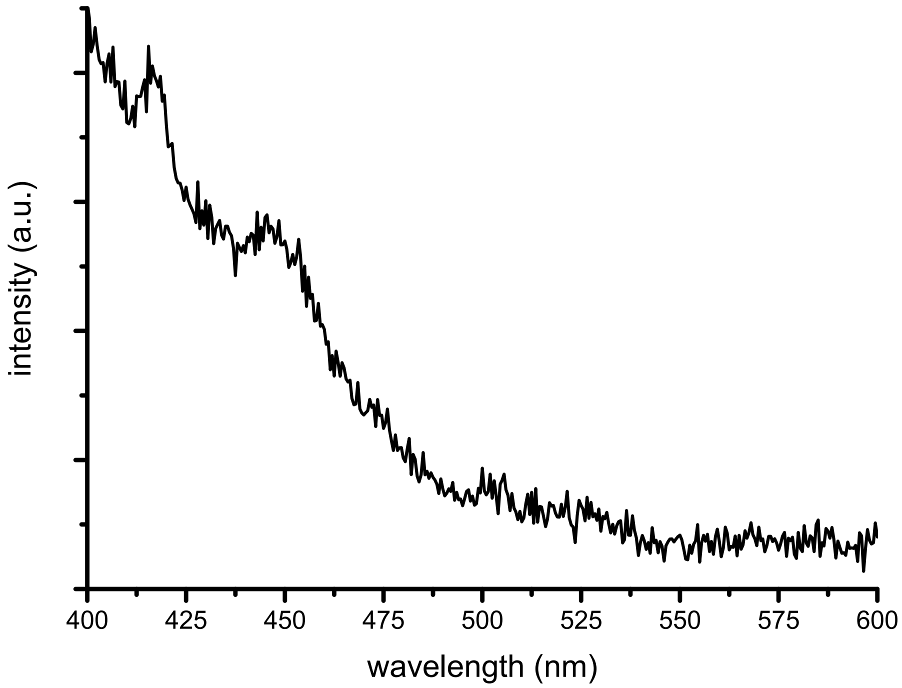


Figure S33. Excitation spectrum of $^{241}Am^{3+}$ incorporated minerals at room temperature (λ_{em} = 687 nm).

Mineral	**ν_1(U=O) cm^{-1}**	**ν_3(U=O) cm^{-1}**	**d(U=O)$_{raman}$ (Å)**	**d(U=O)$_{IR}$ (Å)**	**d(U=O)$_{badgers}$ (Å)**	***f* mdyne Å^{-1}**
Becquerelite	796 829	872 908	1.815 1.782	1.805 1.779	1.774 1.758	5.714 6.196
Becquerelite + Eu	796 822	910	1.815 1.789	1.777	1.760	6.155
andersonite	806 832	913 899	1.779 1.805	1.775 1.785	1.757 1.766	6.252 5.961
Andersonite + Eu	833	895	1.778	1.788	1.760	6.143
grimselite	815	876	1.796	1.802	1.769	5.883
grimselite + Eu	813	901	1.798	1.784	1.764	6.027
Liebigite	829	870 906	1.782	1.807 1.780	1.766	5.954
Liebigite + Eu	829	870 906	1.782	1.807 1.780	1.766	5.954

Table S1. Vibrational data for the mineral and their Eu(III) included complexes and the results of structural analysis.

References

[1] S. Amayri, T. Arnold, H. Förstendorf, G. Geipel, G. Bernhard, *Can. Mineral.* **2004**, *42*, 953-962.

[2] T. Arnold, N. Baumann, *Spectrochim. Acta, Part A: Molecular and Biomolecular Spectroscopy* **2009**, *71A*, 1964-1968.

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[9] Y. Li, P. C. Burns, *Can. Mineral.* **2001**, *39*, 1147-1151.