Supplementary Information for

The Role of Nanoscale Crystallinity on REEs recovery from Coal Fly Ash

*Sheila Gerardo [a], Kevin Matthews [b], Jamie Warner [b], Wen Song [a]**

[a] Center for Subsurface Energy and the Environment, The University of Texas at Austin, Austin, Texas 78712, United States

[b] Texas Materials Institute, The University of Texas at Austin, Austin, Texas 78712, United States

* Corresponding Author: Wen Song; Email: wensong@utexas.edu; Phone: (512) 471-5789

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Table S1- Summarized composition of the ash used in this study [1]. The elemental composition was obtained via ICP-MS analysis of digested ash samples, and the REE-hosting phases were obtained via SEM-EDS microscale visual analysis.

Elemental Composition via ICP-MS	
Elements	**Concentration (ppm)**
Na	12,324 ± 205
Mg	15,190 ± 240
Al	89,438 ± 188
Si	***
K	9,958 ± 52
Ca	43,478 ± 814
Ti	5,285 ± 77
Mn	267 ± 8
Fe	29,464 ± 1332
Sr	1,664 ± 70
Zr	191 ± 7
Ba	3,769 ± 72
Total REEs	384 ± 32

REEs Microscale Spatial Distribution	
REEs-hosting Phases	**Percentage (%)**
Dense Matrix Particles	78
Permeable Matrix Particles	12
Discrete/ Surface-bound REEs	10

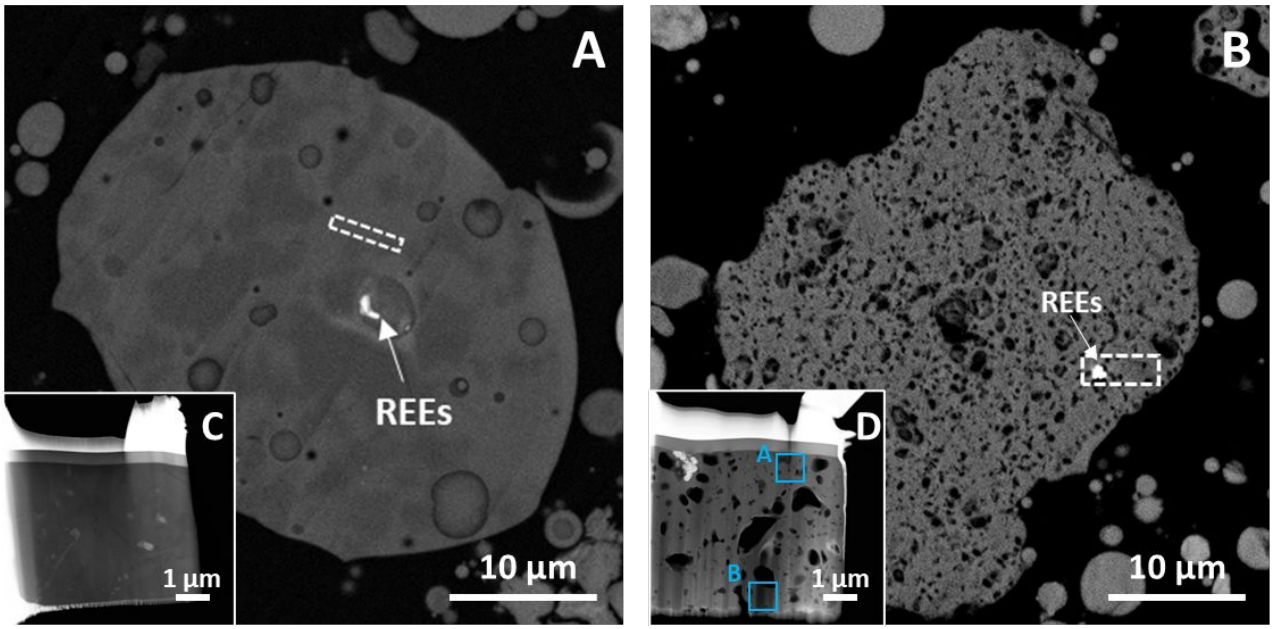

Figure S1- (A) dense matrix particle, and (B) porous matrix particle used in this study (adapted with permission from Gerardo et al. 2022 [1]. Copyright 2022 American Chemical Society). Dashed boxes show the location where TEM lamellas were sectioned off. (C and D) Insets show STEM images of the dense and porous matrix lamellas, respectively, providing insight into the plane normal to the one shown in (A) and (B). The blue boxes highlighted in (D) indicate where the TEM images depicted in Figure S7 were acquired.

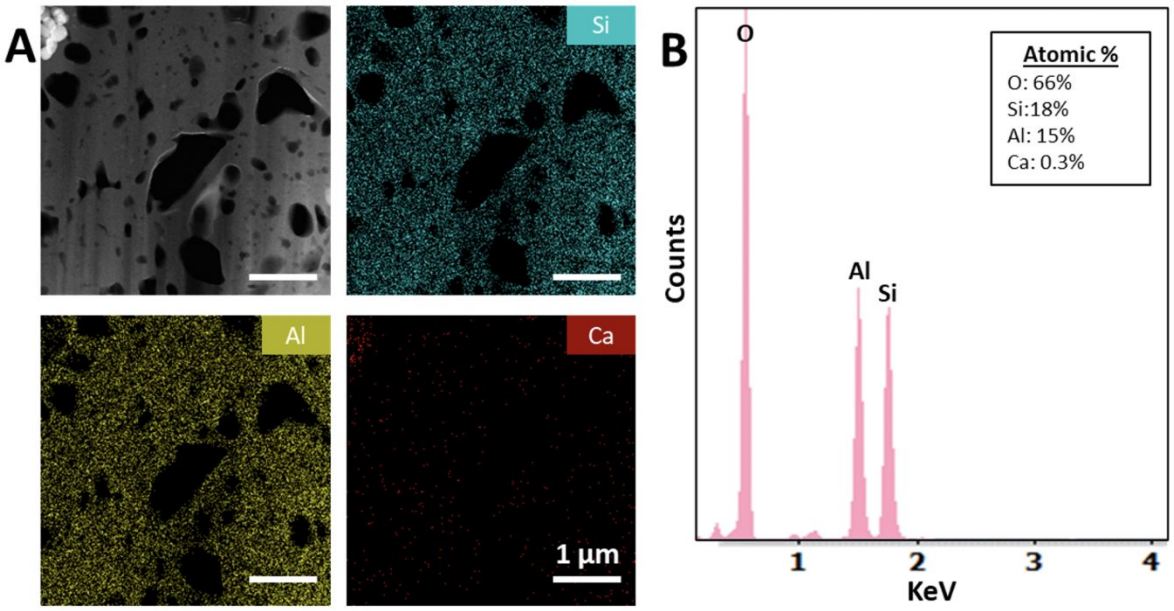

Figure S2- (A) STEM-EDS maps of the porous matrix lamella for silicon (blue), aluminum (yellow), and calcium (red). (B) Corresponding EDS spectra and semi-quantitative elemental composition (i.e., not calibrated against standards).

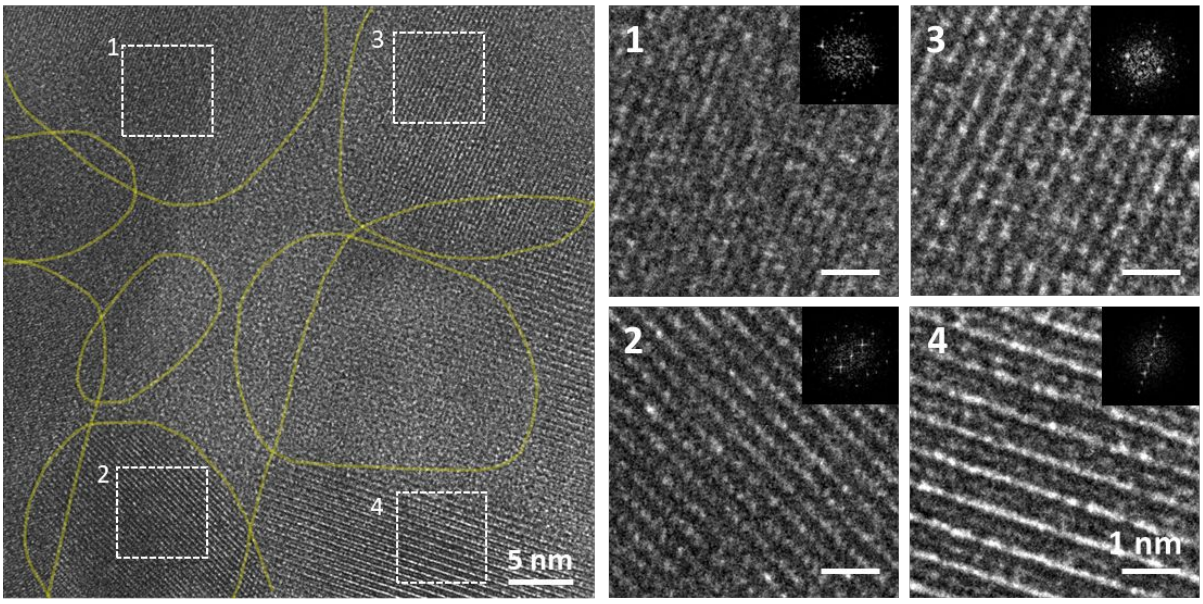

Figure S3- HRTEM of the polycrystalline porous lamella. Yellow lines delineate the observed nanograins, and white boxes indicate the location where the high magnification images of each grain were taken. Images for the grains not depicted here can be found in the main text. The insets of figures 1-4 correspond to the calculated FFT patterns used to determine the d-spacing of each grain.

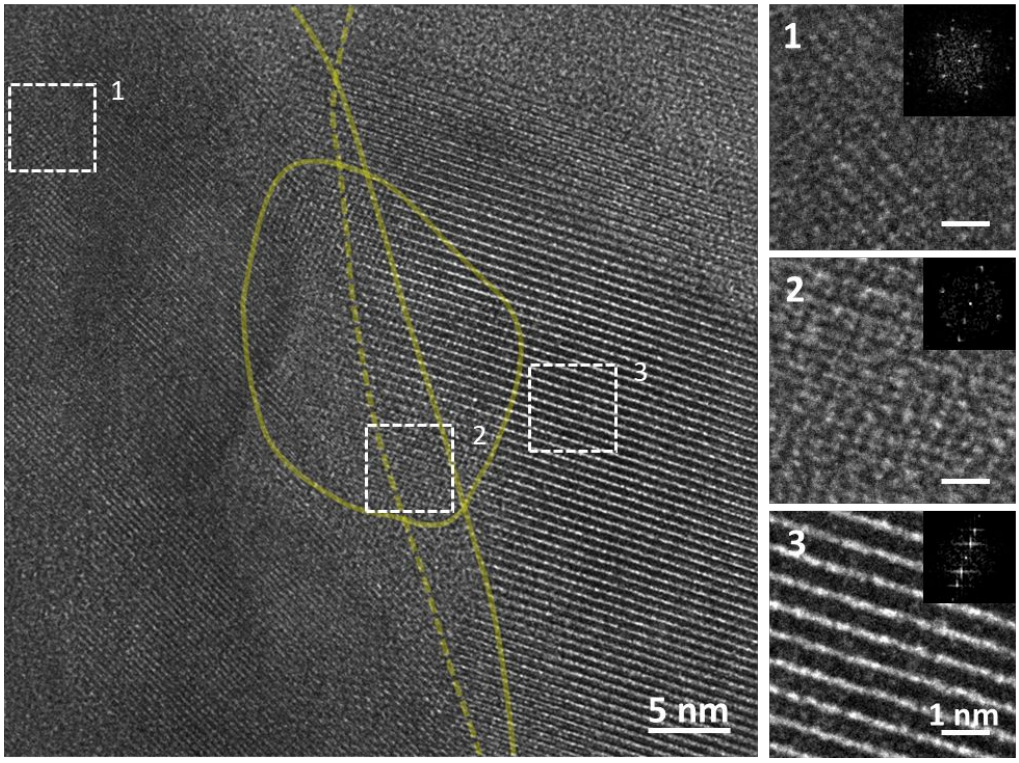

Figure S4- HRTEM of the polycrystalline porous lamella, collected below the location showcased on figure S3. Yellow lines delineate the observed nanograins, and white boxes indicate the location where the high magnification images of each grain were taken. The insets of figures 1-3 correspond to the calculated FFT patterns used to determine the d-spacing of each grain.

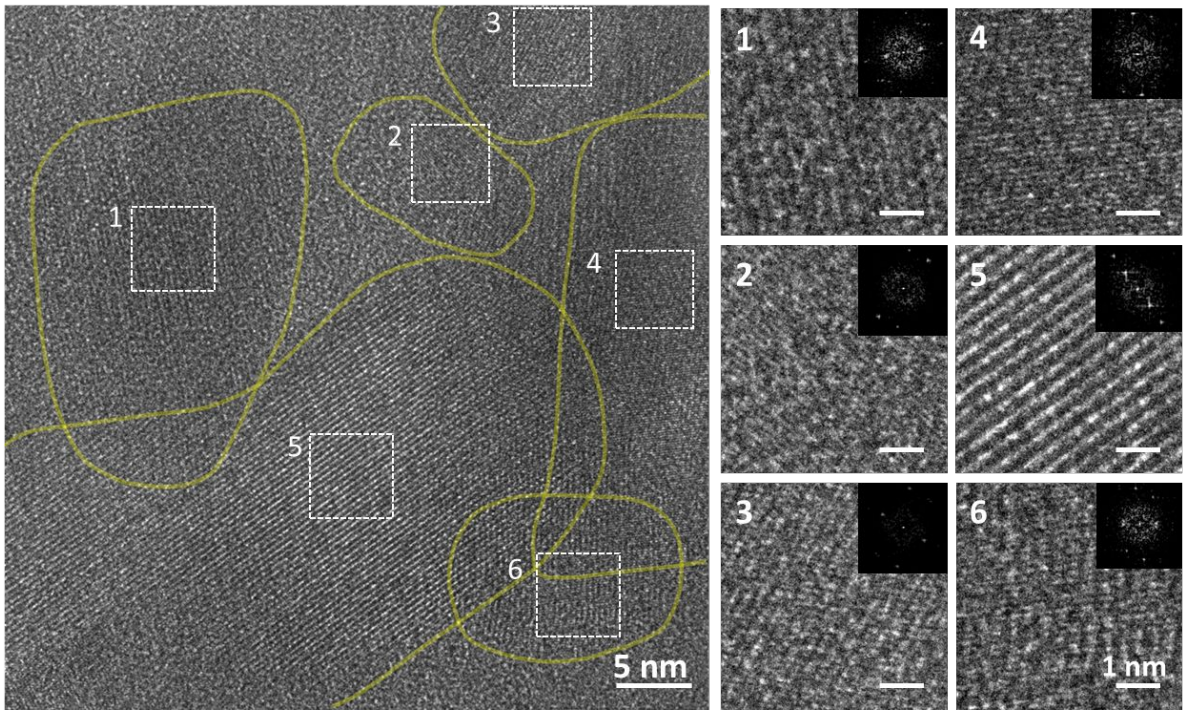

Figure S5- HRTEM of the polycrystalline porous lamella. Yellow lines delineate the observed nanograins, and white boxes indicate the location where the high magnification images of each grain were taken. The insets of figures 1-6 correspond to the calculated FFT patterns used to determine the d-spacing of each grain.

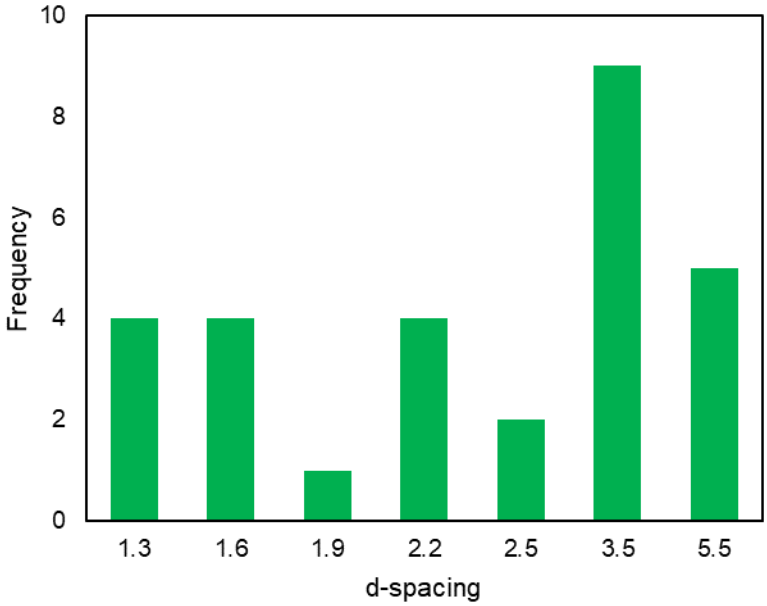

Figure S6-Frequency plot for d-spacing values calculated using the FFT patterns shown in figures S3-S5.

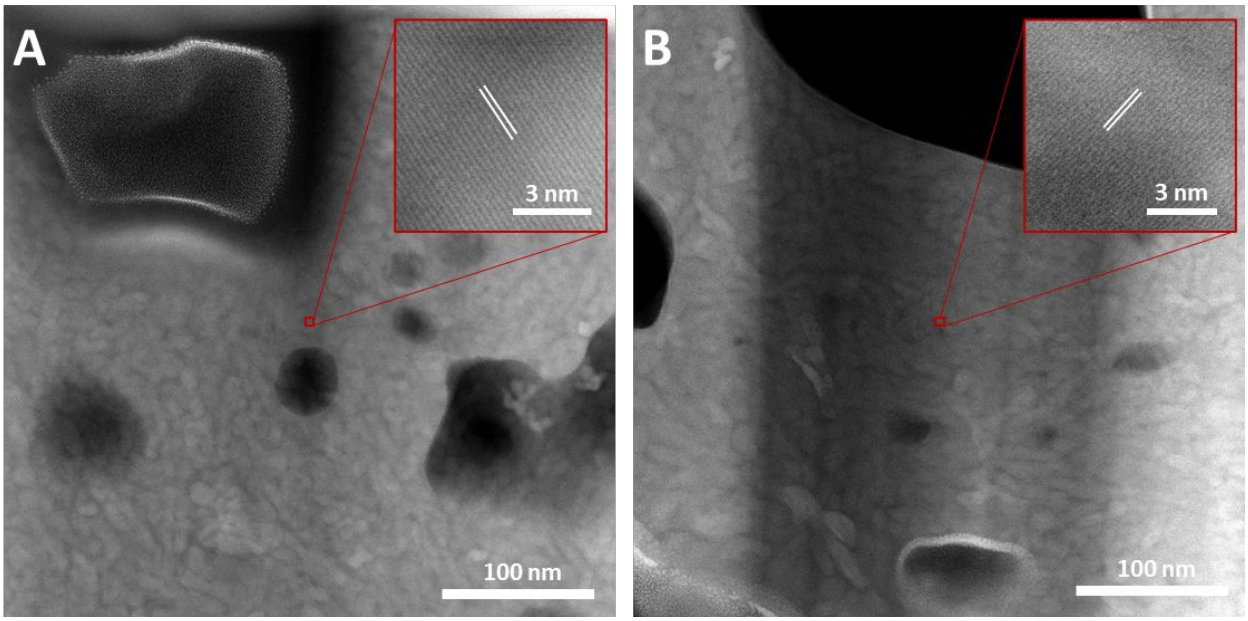

Figure S7- (A and B) STEM images collected from the porous matrix lamella, showing nanocrystals throughout the matrix. Inset images showcase crystal lattice fringes observed in STEM mode. The location where Figures A and B were collected is highlighted in Figure S1D.

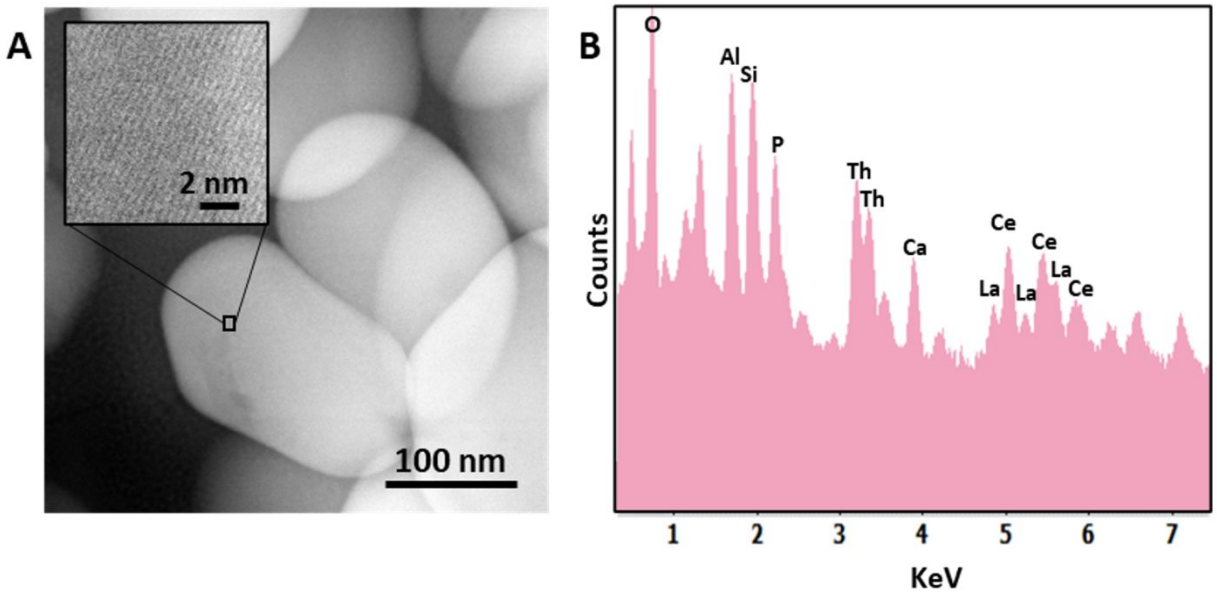

Figure S8-(A) STEM image of REE-bearing minerals, with lattice fringes visible at higher magnifications as shown in the inset image. (B) EDS spectra of the REE-bearing minerals, indicating that they consist of phosphate grains. Counts are plotted in log scale.

References

1. Gerardo, S.; Davletshin, A. R.; Loewy, S. L.; Song, W. From Ashes to Riches: Microscale Phenomena Controlling Rare Earths Recovery from Coal Fly Ash. *Environmental Science & Technology* **2022**, 56 (22), 16200–16208. DOI: 10.1021/acs.est.2c04201