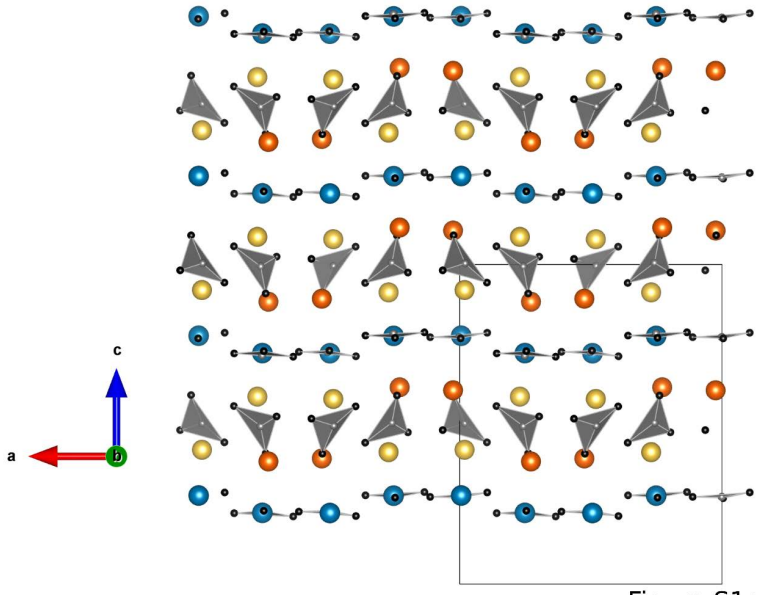



Figure S1a

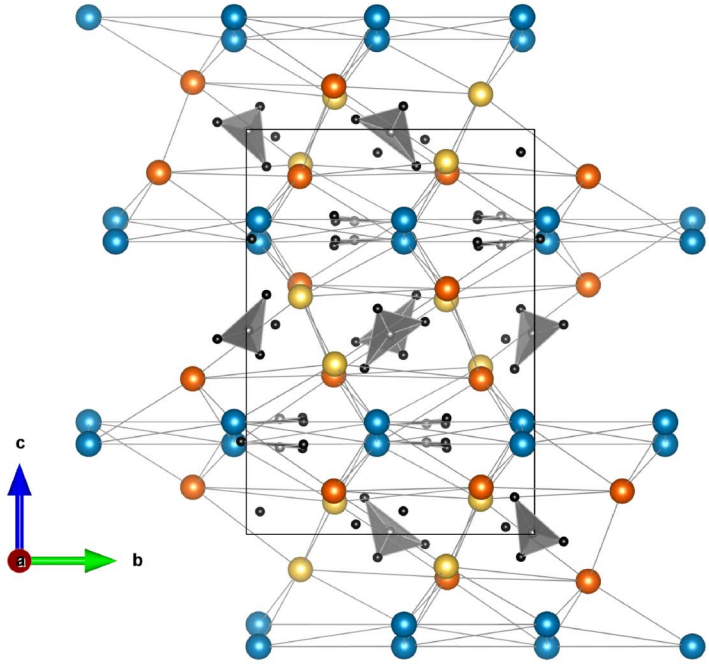



Figure S1b

**FIGURE S1.** Crystal structure of nyerereite (**a**) along the (010) direction and (**b**) showed as an anion-stuffed cation array along the (100) direction where lines represent imaginary junctions between cations (after Gavryushkin et al. 2016). Colors are as follows: blue is $Ca^{[9]}$, yellow is $Na1^{[8]}$, orange is $Na2^{[6]}$, black is O, gray is C. The almost planar $CO_3^{2-}$ groups are also shown.

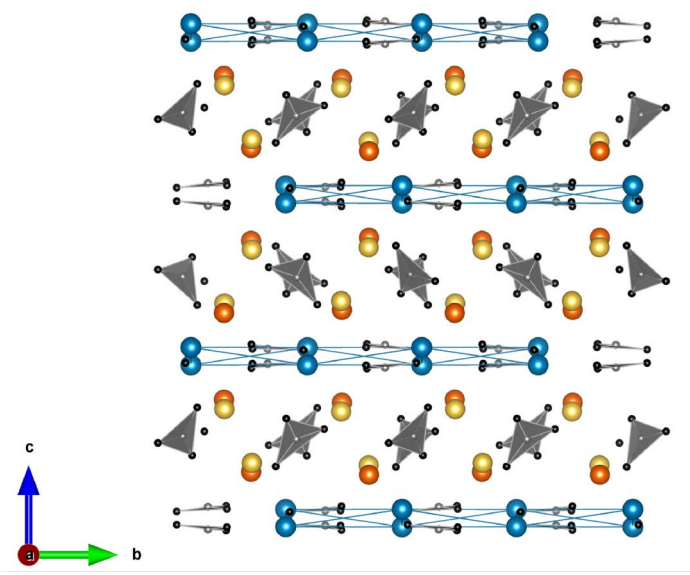



Figure S2a

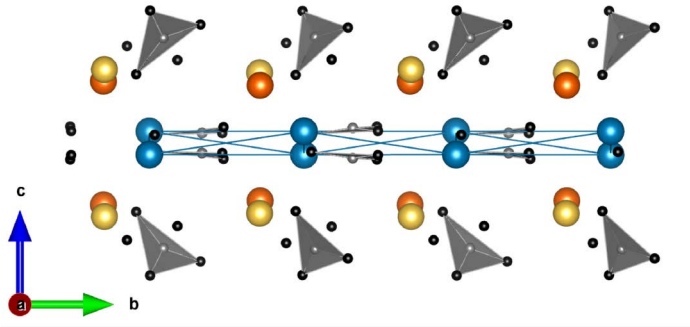



Figure S2b

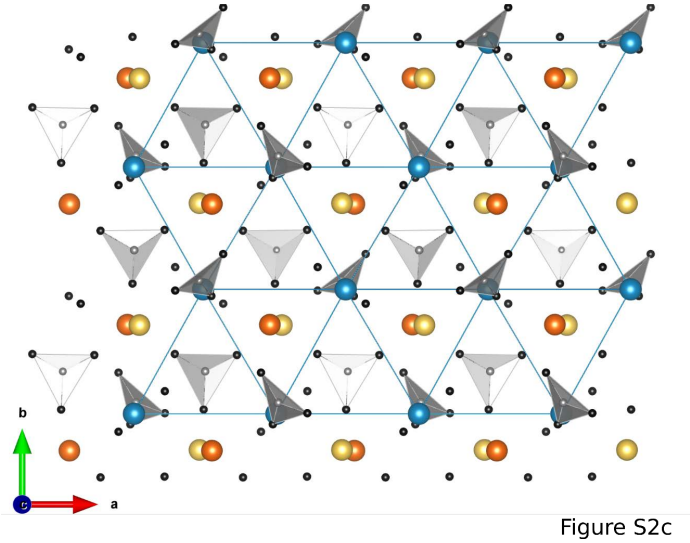



Figure S2c

**FIGURE S2.** Crystal structure of nyerereite in the *bc* plane (**a**). Isolated portion of the 3D framework in the *bc* (**b**) and ab planes (**c**). In (**c**) the 2D framework generated by the $[CaCO_3]^{-x}$ units is shown by the blue lines representing the imaginary connections between the Ca atoms (after Song et al. 2017). Colors are as follows: blue is Ca[9], yellow is Na1[8], orange is Na2[6], black is O, gray is C. The almost plana $CO_3^{2-}$ groups are also shown.

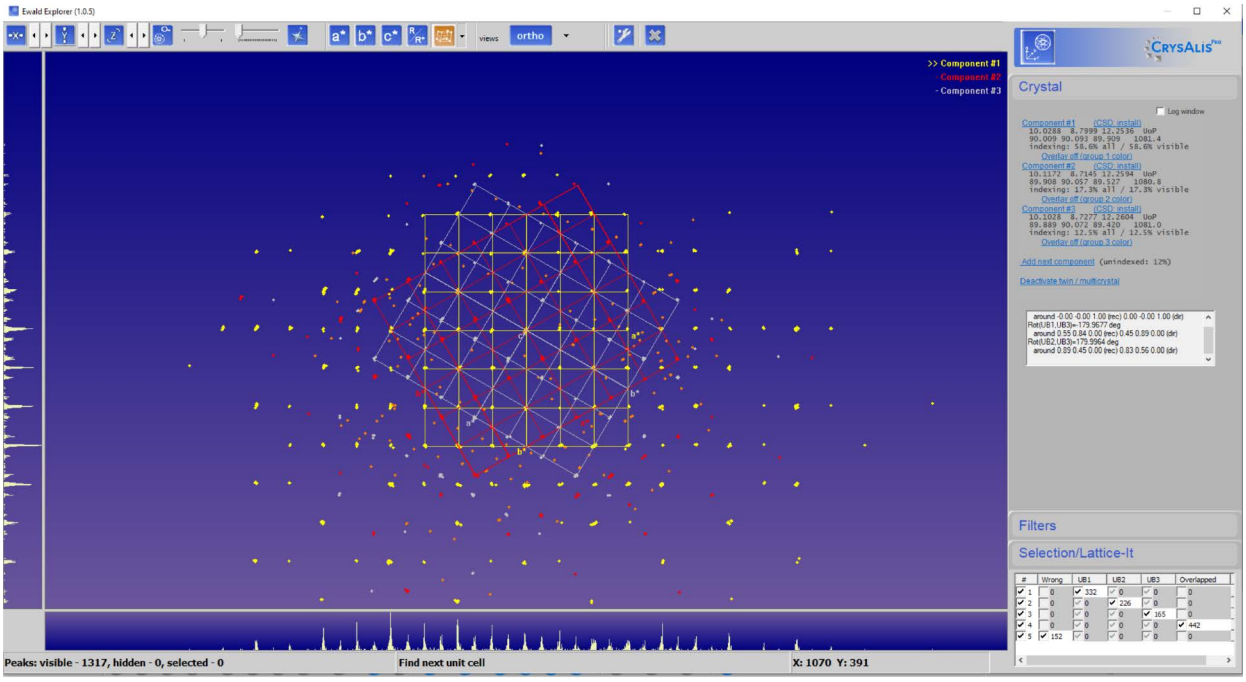
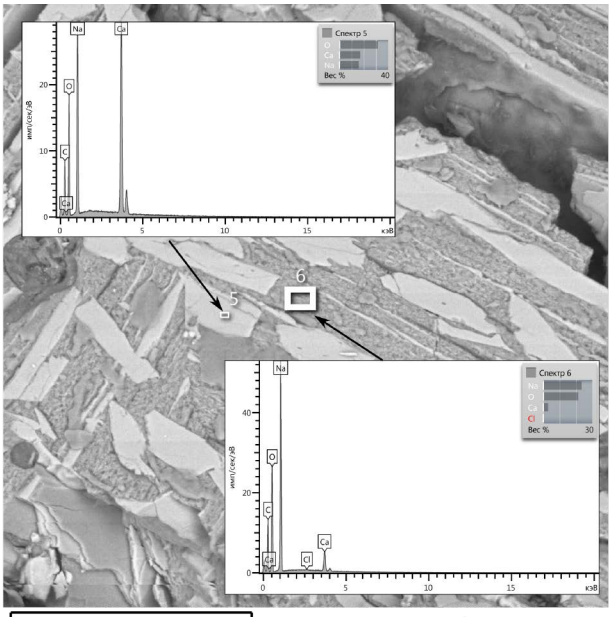
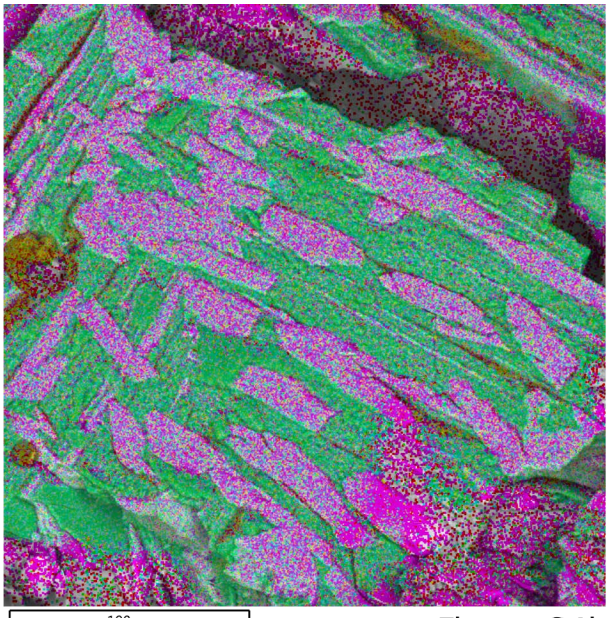
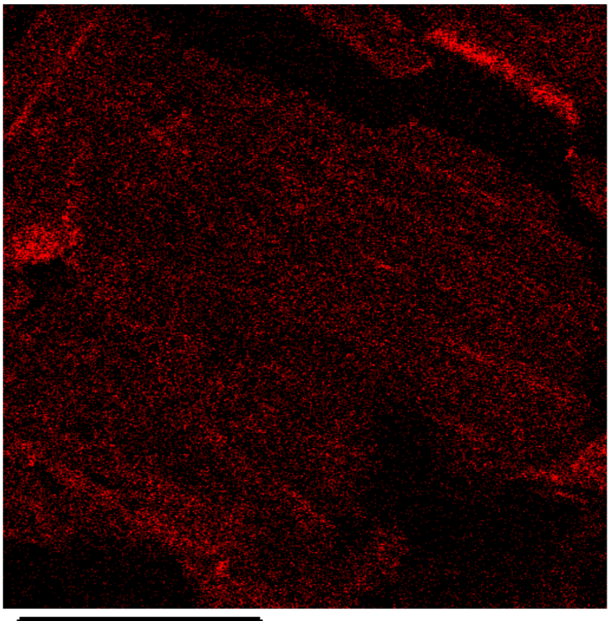



Figure S3

**FIGURE S3.** Collected data extraction and unit cells used for reflection indexing of hydrothermal nyerereite.



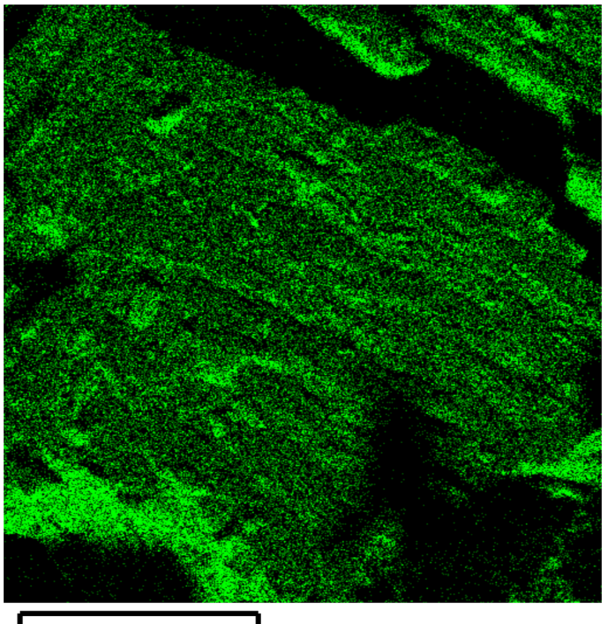




**FIGURE S4.** Backscattered electrons (BSE) images and EDS X-ray maps recorded on selected portions of NMAG (**a–f**) and NHD15 (**g–l**). BSE images are shown in (**a**, **g**); whereas, results of the EDS analysis are shown in (**b**, **h**). The separate maps for each element are reported for C (**c**, **i**), O (**d**, **j**), Na (**e**, **k**), Ca (**f**, **l**).

*(Continued on next page)*

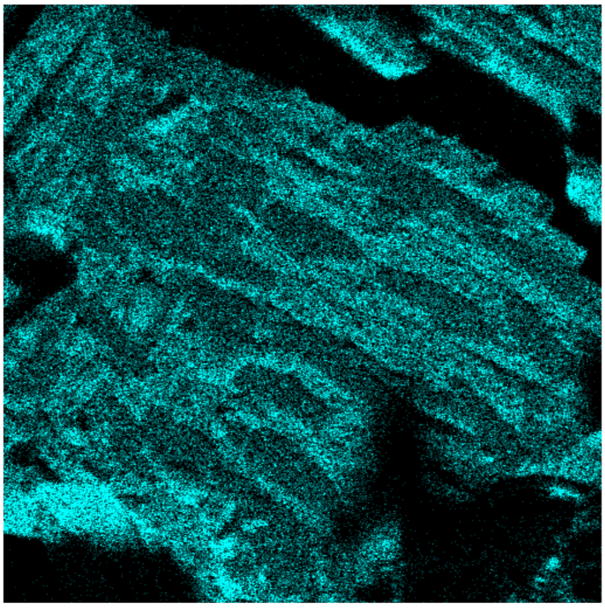



Figure S4e

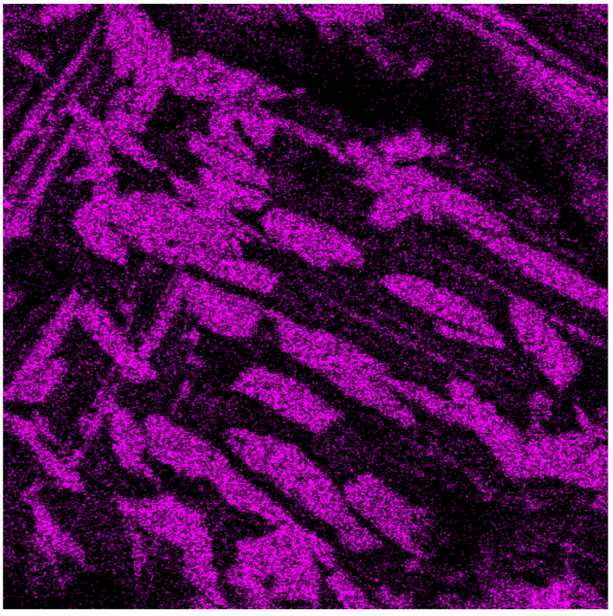



Figure S4f

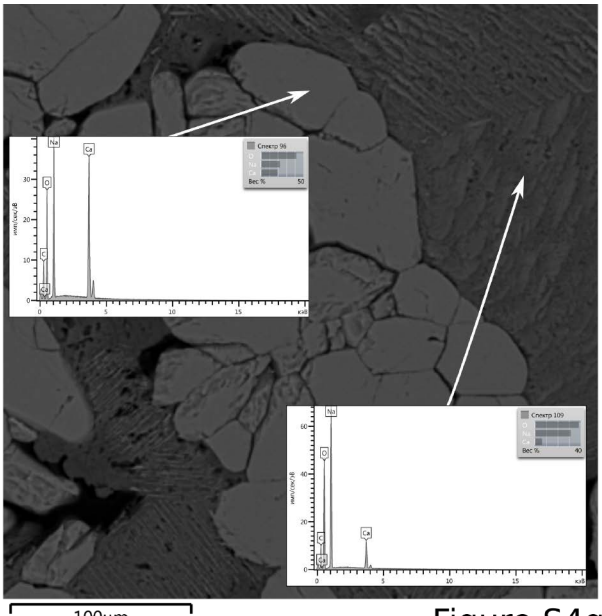



Figure S4g

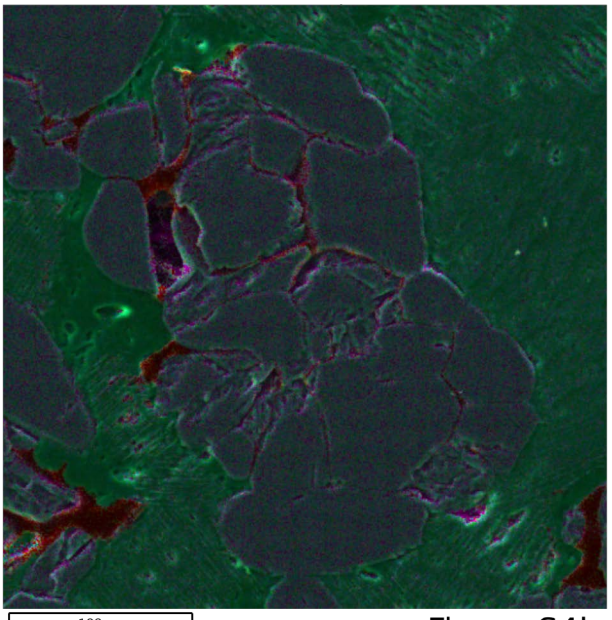



Figure S4h

**FIGURE S4.—*CONTINUED***

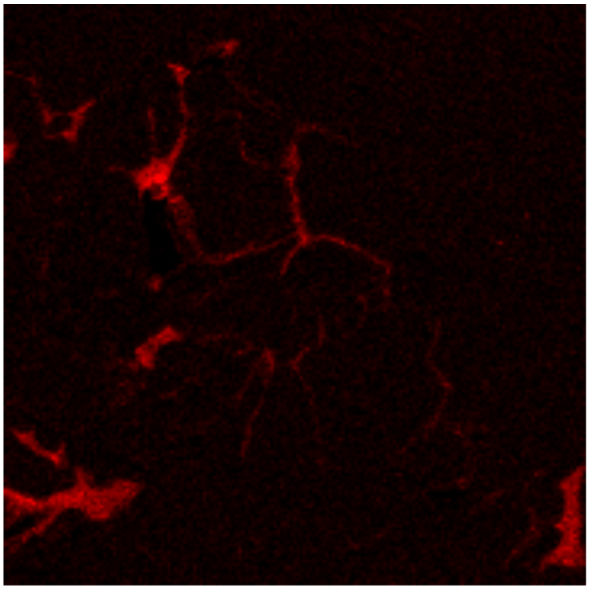



Figure S4i

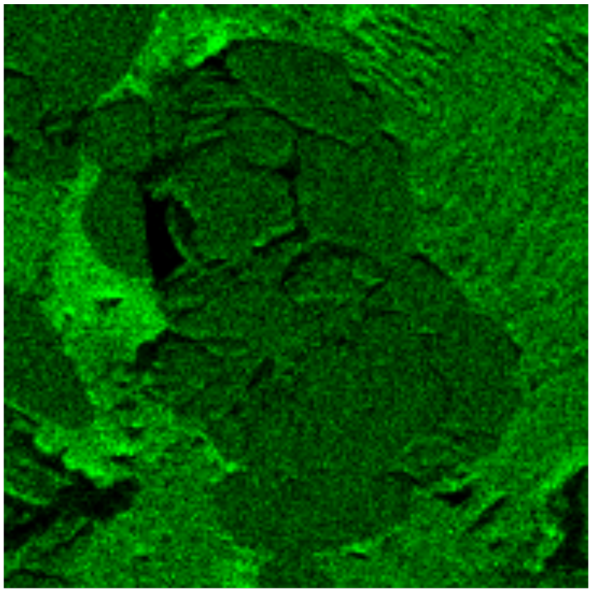



Figure S4j

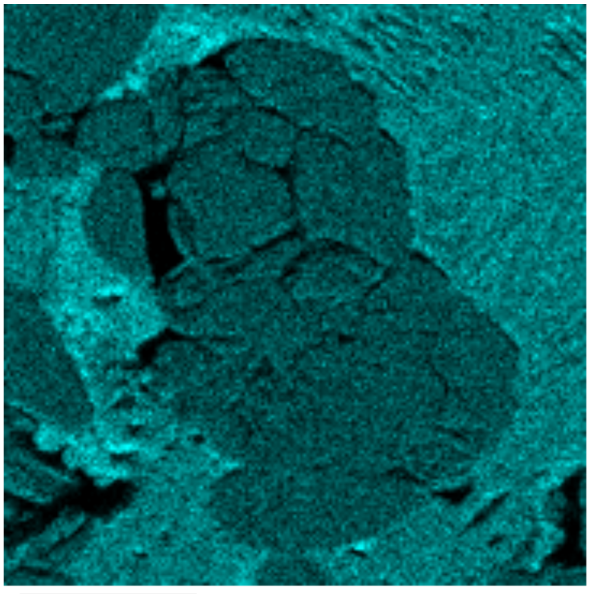



Figure S4k

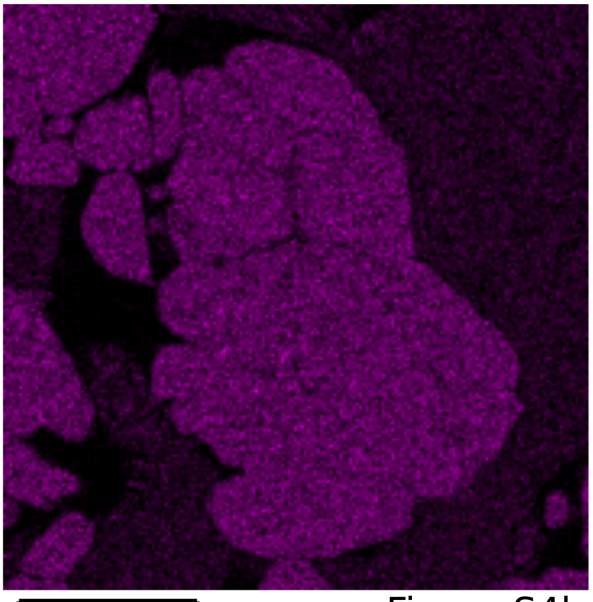



Figure S4l

**FIGURE S4.**—***CONTINUED***