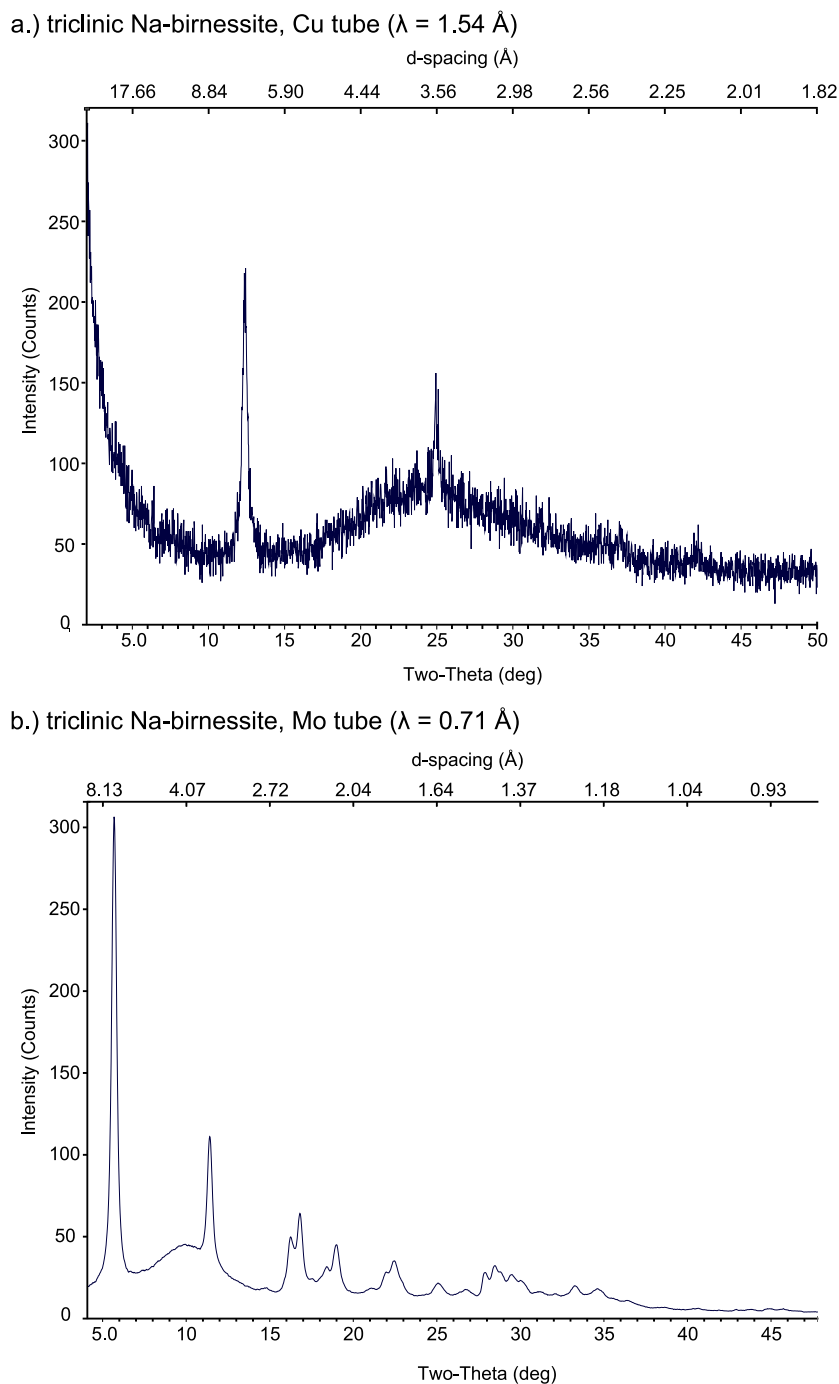


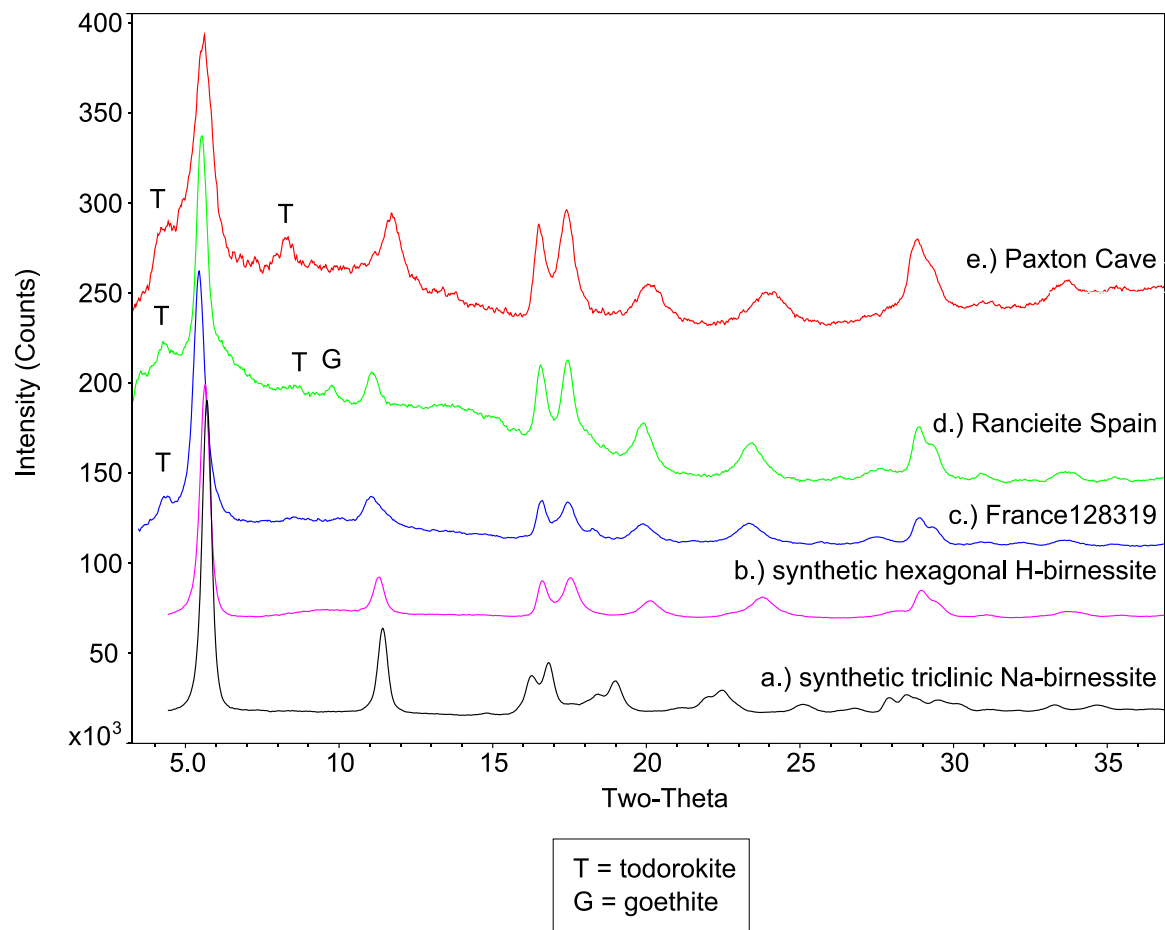
### SUPPLEMENTARY INFORMATION (SI)



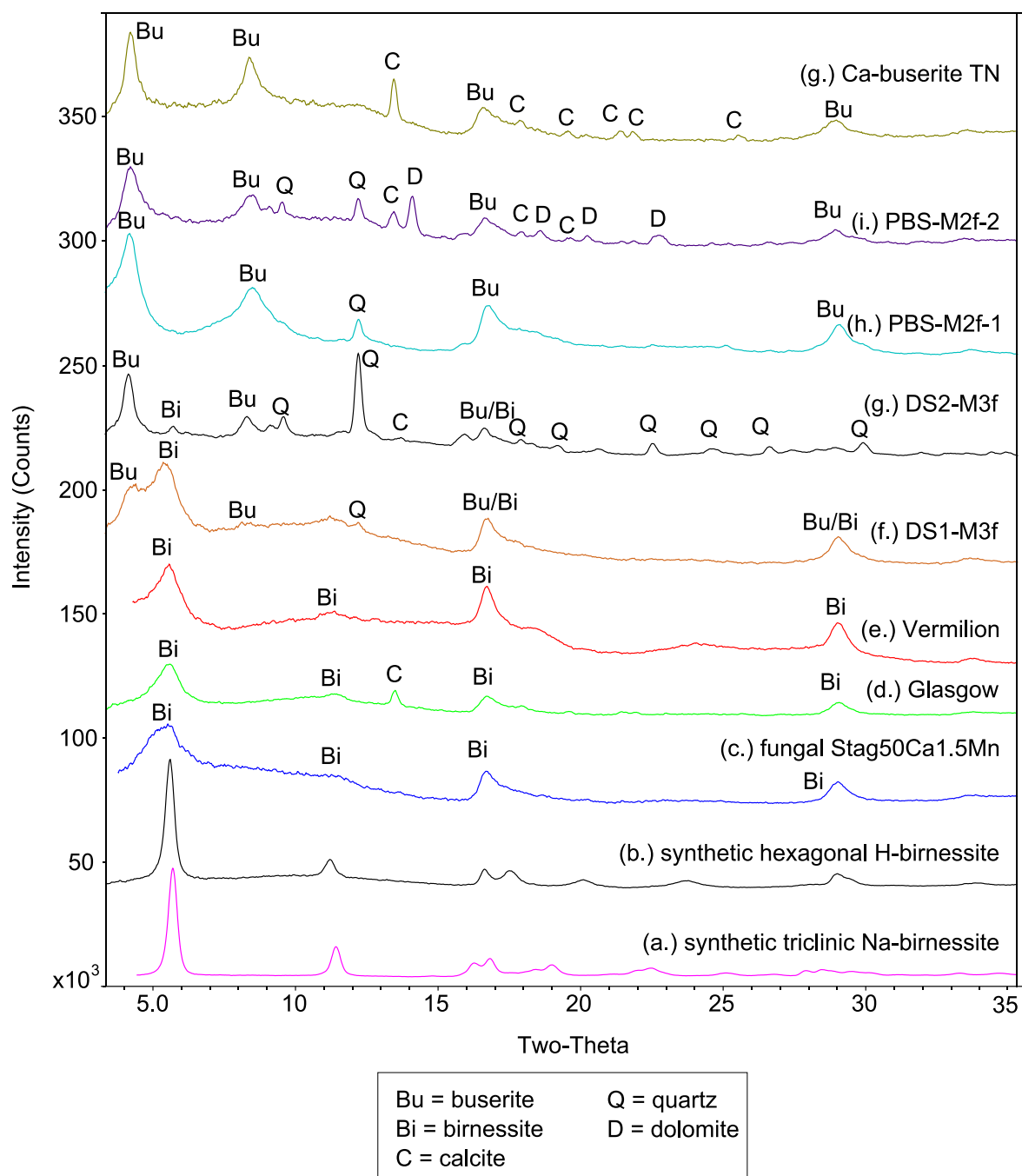
**Fig. 1.** XRD pattern of the same synthetic triclinic Na-birnessite using a (a) Cu tube and (b) Mo tube during data collection for Debye-Scherrer geometry imaging plate diffractometer.



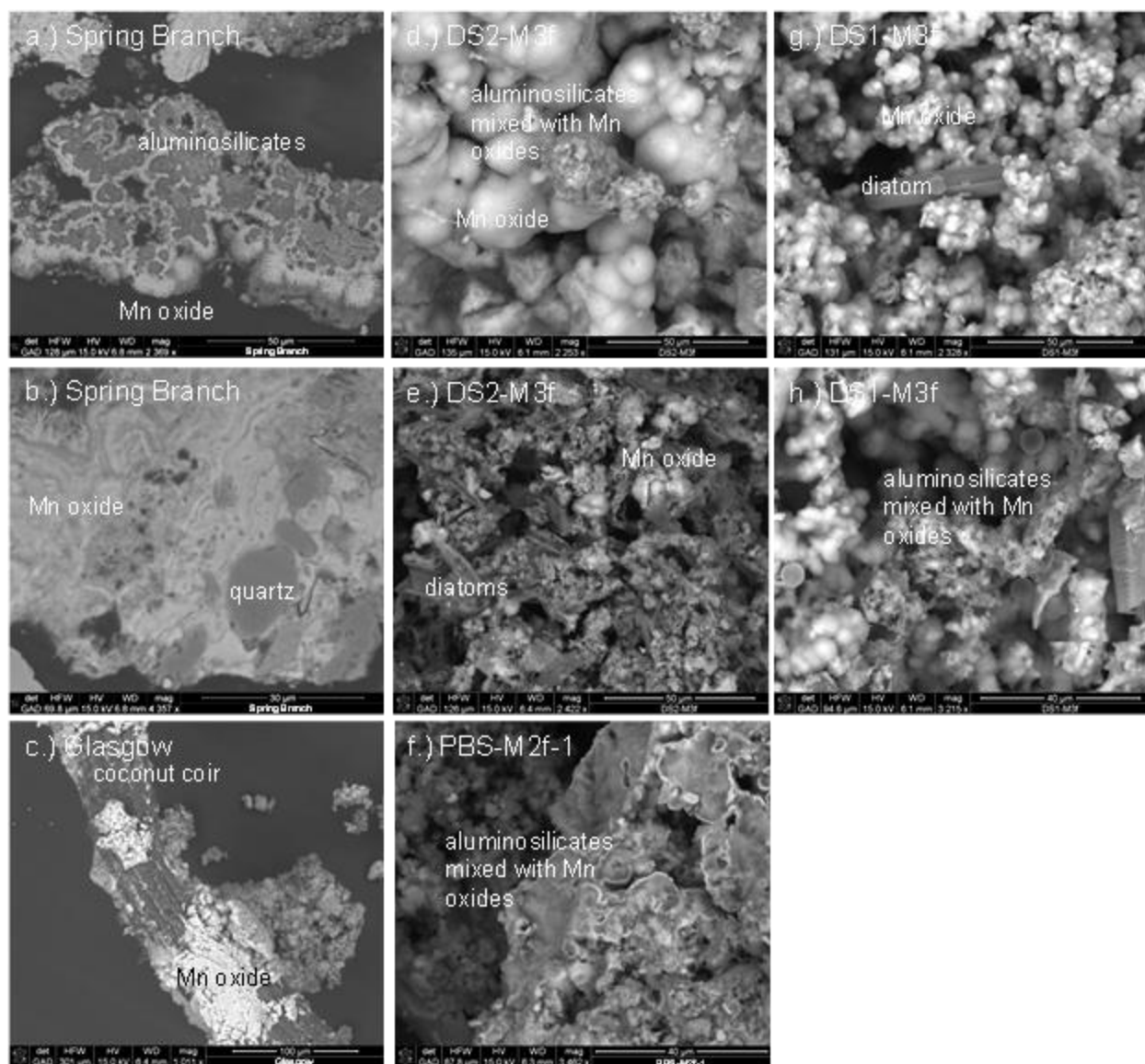
**Fig. 2.** Metal removal units. A metal removal unit at the passive coal mine drainage treatment site near Glasgow, PA.



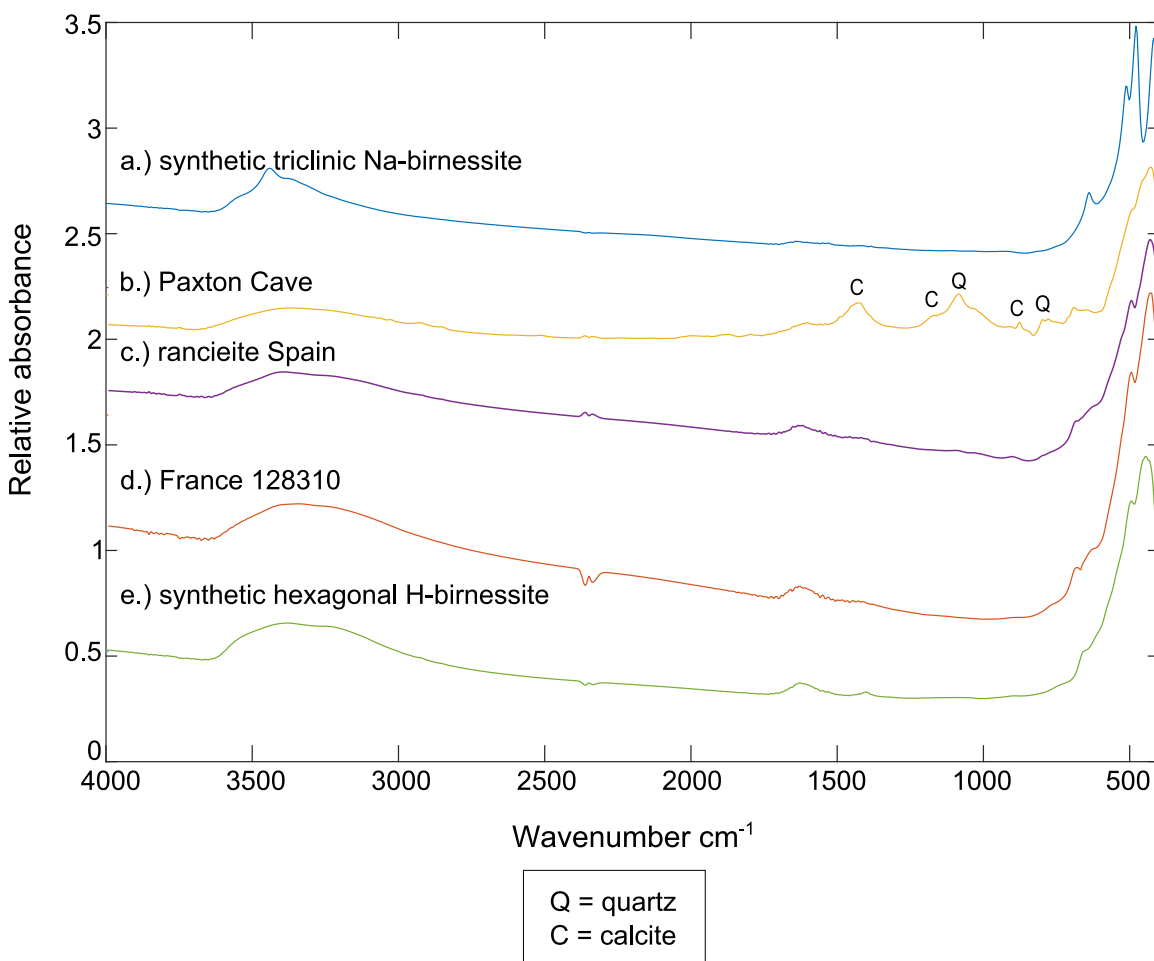
**Fig. 3.** XRD of all well-crystalline birnessites with non-birnessite phases labeled.



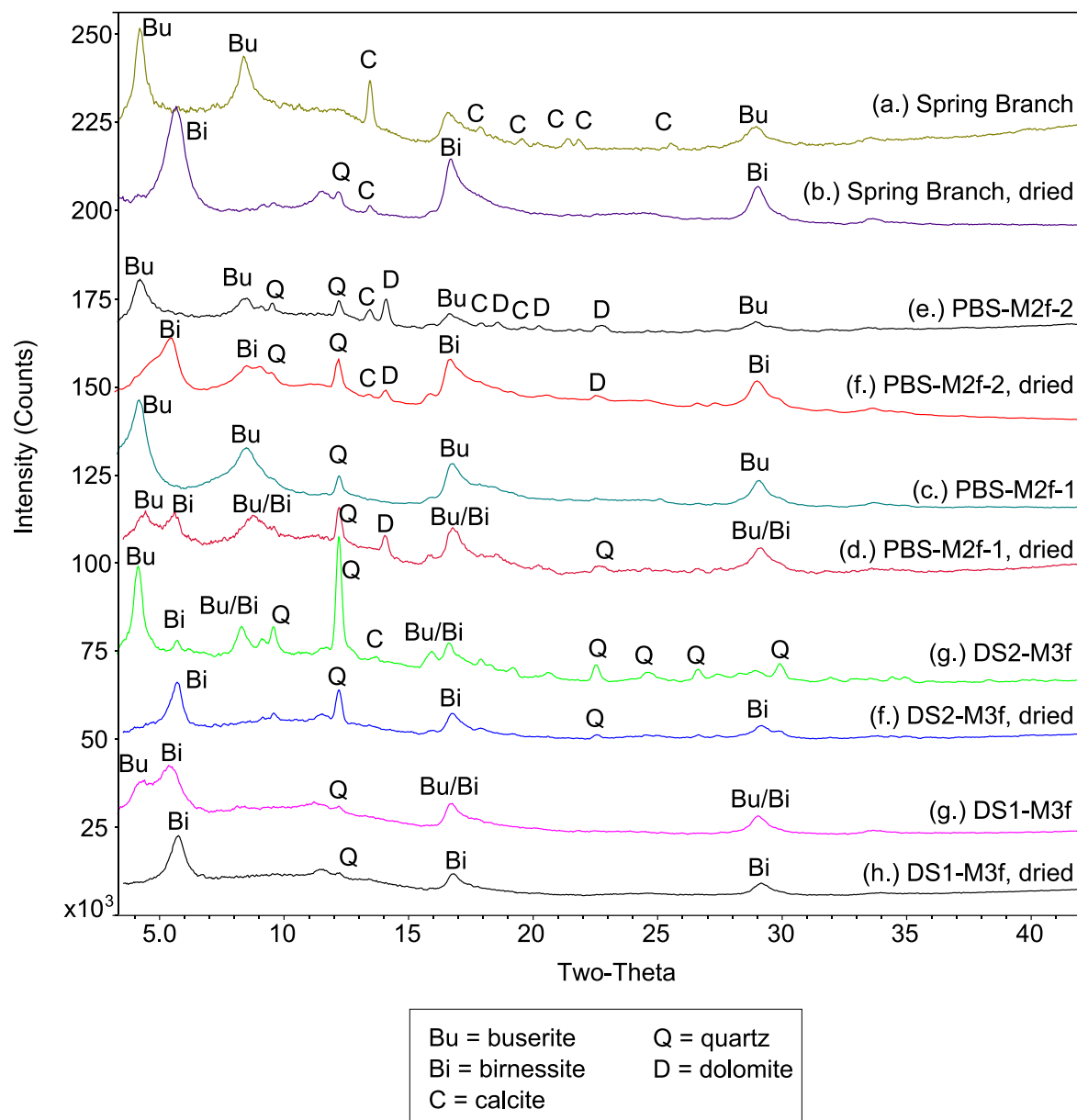
**Fig. 4.** XRD of all poorly-crystalline birnessites.



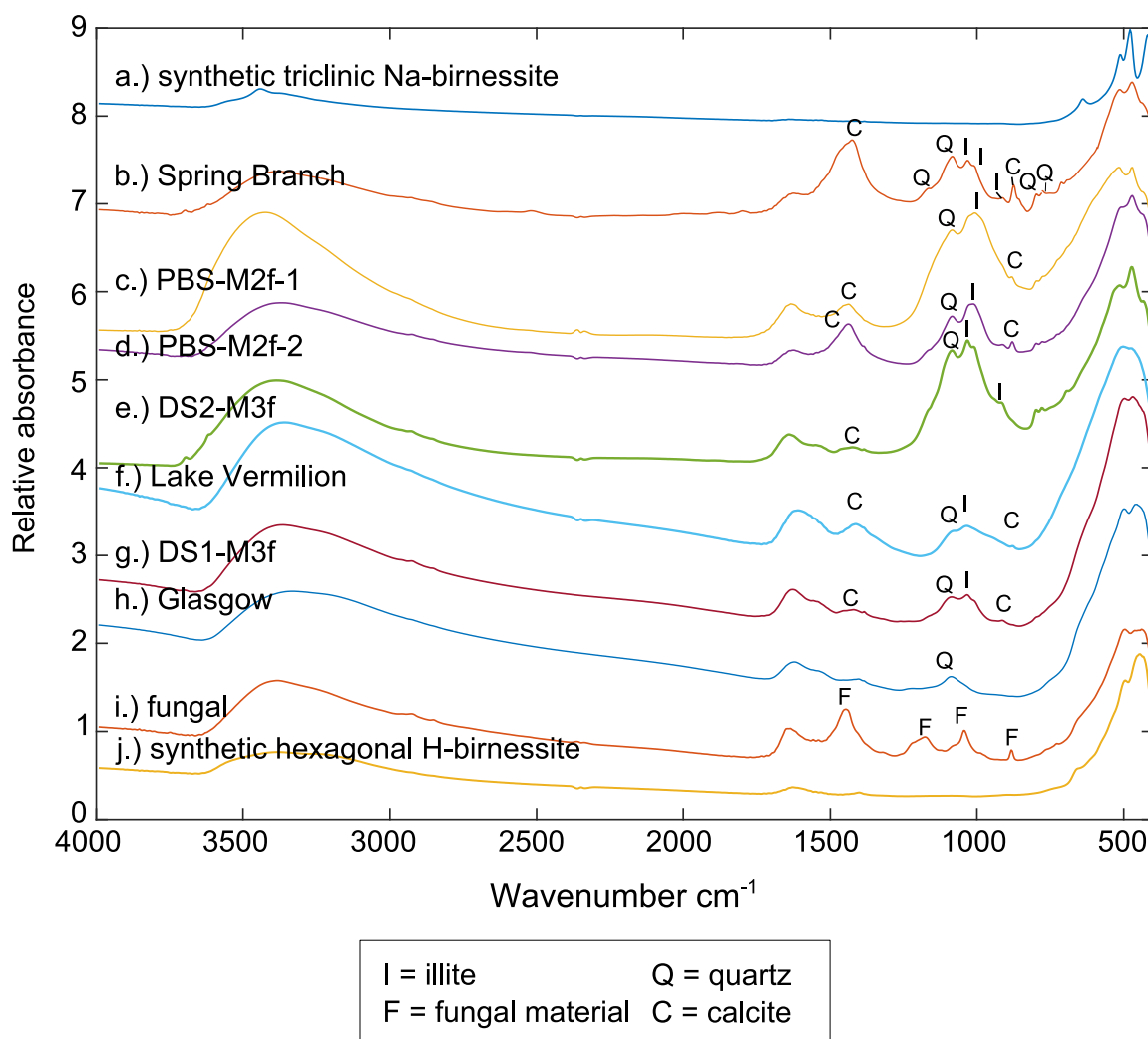
**Fig. 5.** Additional SEM images of natural Mn oxides.



**Fig. 6.** Full FTIR spectra of well-crystalline samples with non-birnessite phases labeled.

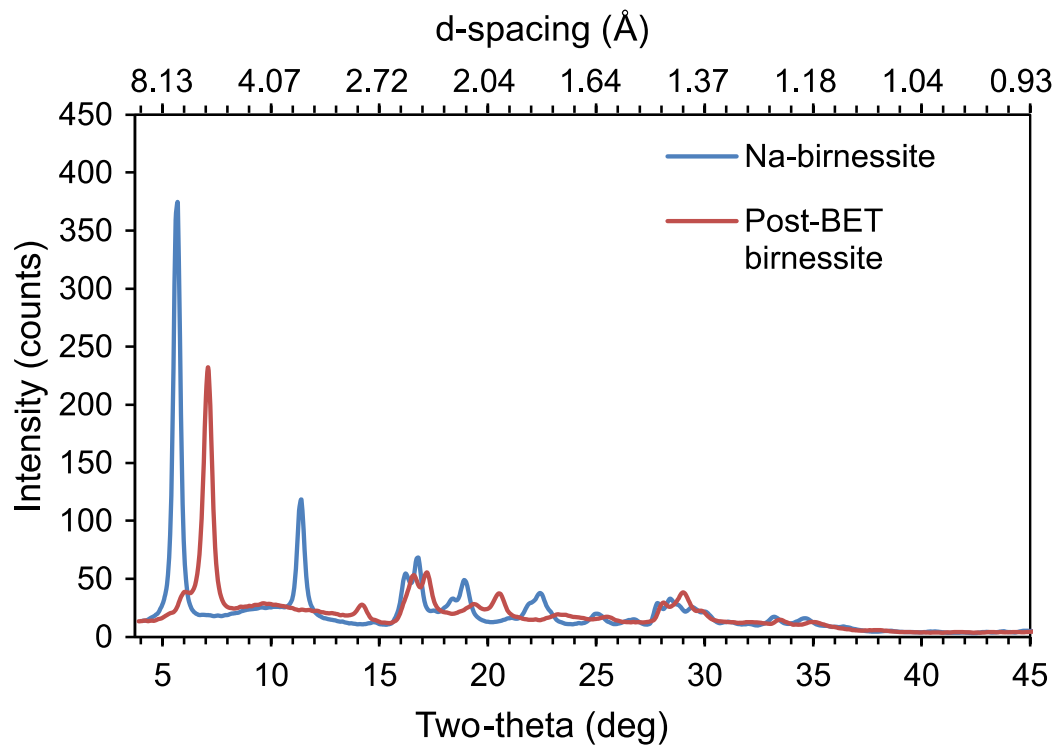


**Fig. 7.** XRD of original buserites and dehydrated buserites.

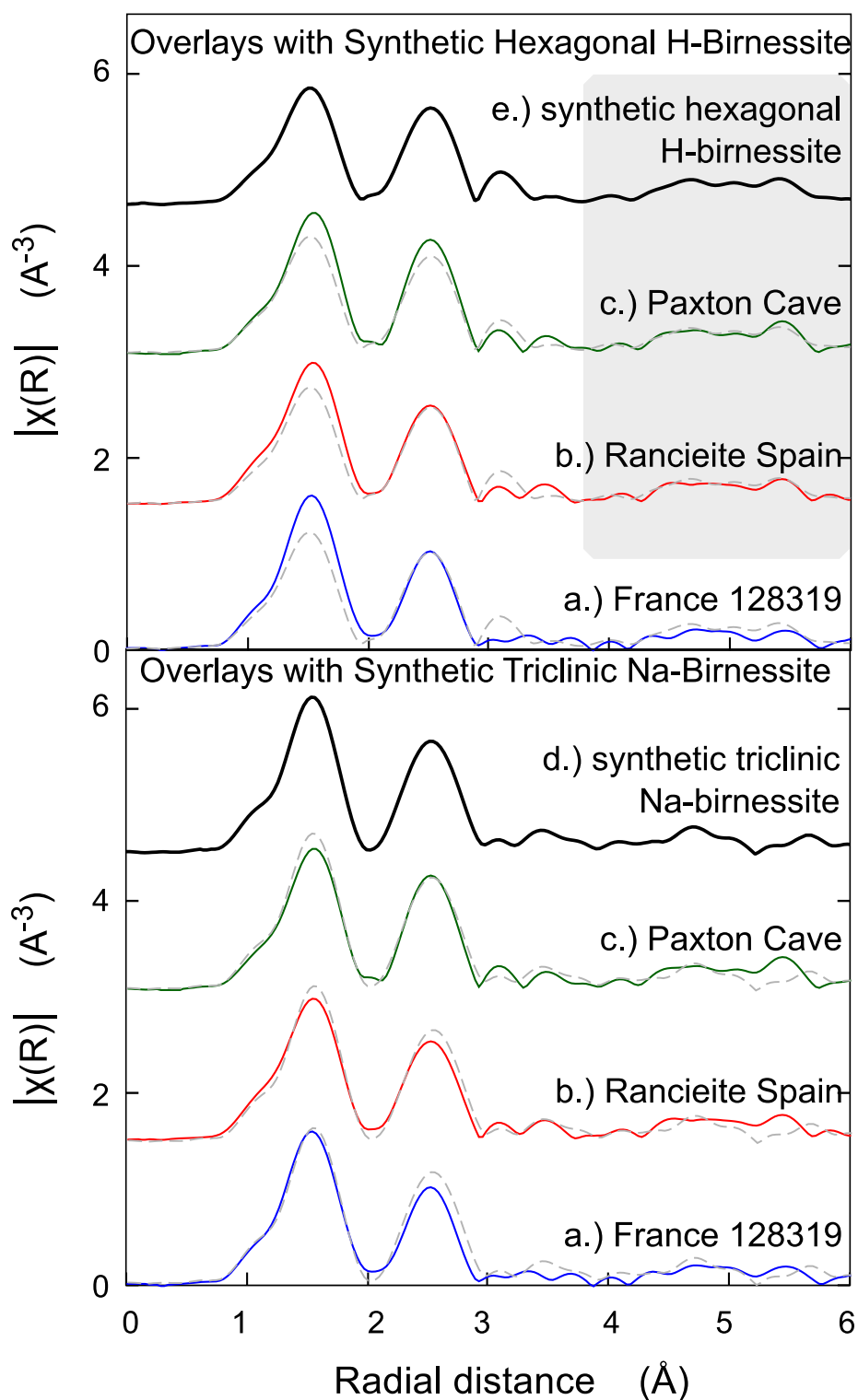


**Fig. 8.** Full FTIR of poorly-crystalline samples, with non-birnessite phases labeled.





**Fig. 9.** BET analysis of triclinic Na-birnessite led to a change in the birnessite structure and a specific surface area value of 47.53 m<sup>2</sup>/g.



**Fig. 10.** Radial distribution functions (RDFs) of XRD-identified hexagonal birnessite with overlays of synthetic triclinic Na-birnessite and synthetic hexagonal H-birnessite RDFs.

**Table 1.** Principal component analysis using  $k^2$ -weighted  $\chi(k)$  spectra.

Sample	Eigenvalues	Variance	Cumulative variance
1	10.603	0.964	0.964
2	0.115	0.010	0.974
3	0.094	0.009	0.983
4	0.049	0.004	0.987
5	0.041	0.004	0.991
6	0.031	0.003	0.994
7	0.023	0.002	0.996
8	0.017	0.002	0.997
9	0.011	0.001	0.998
10	0.011	0.001	0.999
11	0.006	0.001	1.000

**Table 2.** LCF results of XANES region for Mn oxidation states using rhodochrosite or manganosite, manganite, and pyrolusite standards.

Sample	Mn <sup>4+</sup>	Mn <sup>3+</sup>	Mn <sup>2+</sup>	XANES R-factor	Ave
XANES Triclinic Na-birn <sup>*</sup>	0.65	0.35	0.00	0.0066758	3.65
XANES Triclinic Na-birn <sup>+</sup>	0.62	0.38	0.00	0.0069252	3.62
XPS Triclinic Na-birn	0.60	0.38	0.02		3.58
XANES H-Birn pH 2 <sup>*</sup>	0.73	0.19	0.09	0.0066686	3.63
XANES H-Birn pH 2 <sup>+</sup>	0.50	0.44	0.06	0.0036993	3.45
XPS H-Birn pH 2	0.68	0.22	0.10		3.58
XANES Glasgow <sup>*</sup>	0.61	0.26	0.14	0.0023065	3.47
XANES Glasgow <sup>+</sup>	0.48	0.48	0.34	0.0037540	3.44
XPS Glasgow	0.60	0.23	0.17		3.43
XANES Paxton Cave <sup>*</sup>	0.93	0.06	0.01	0.0056636	3.92
XANES Paxton Cave <sup>+</sup>	0.82	0.18	0.00	0.0065921	3.82
XPS Paxton Cave	0.91	0.00	0.09		3.82
XANES Spring Branch <sup>*</sup>	0.75	0.21	0.04	0.0045350	3.68
XANES Spring Branch <sup>+</sup>	0.59	0.41	0.00	0.0049559	3.59
XPS Spring Branch	0.58	0.37	0.05		3.53
XANES PBS-M2f-2 <sup>*</sup>	0.71	0.27	0.03	0.0021596	3.68
XANES PBS-M2f-1 <sup>*</sup>	0.71	0.26	0.03	0.0010731	3.69
XANES DS2-M3f <sup>*</sup>	0.73	0.24	0.04	0.0045557	3.69
XANES Vermilion <sup>*</sup>	0.60	0.34	0.07	0.0013238	3.49
XANES DS1-M3f <sup>*</sup>	0.69	0.22	0.08	0.0025410	3.61
XANES Stag50Ca1p5Mn <sup>*</sup>	0.69	0.17	0.14	0.0027844	3.55
XANES France 128319 <sup>*</sup>	0.77	0.23	0.00	0.0056115	3.77
XANES rancieite Spain <sup>*</sup>	0.78	0.21	0.01	0.0021152	3.76

<sup>\*</sup>rhodochrosite, manganite, and pyrolusite standards

<sup>+</sup>manganosite, manganite, and pyrolusite standards