

FIGURE S1.—Continued on next page.

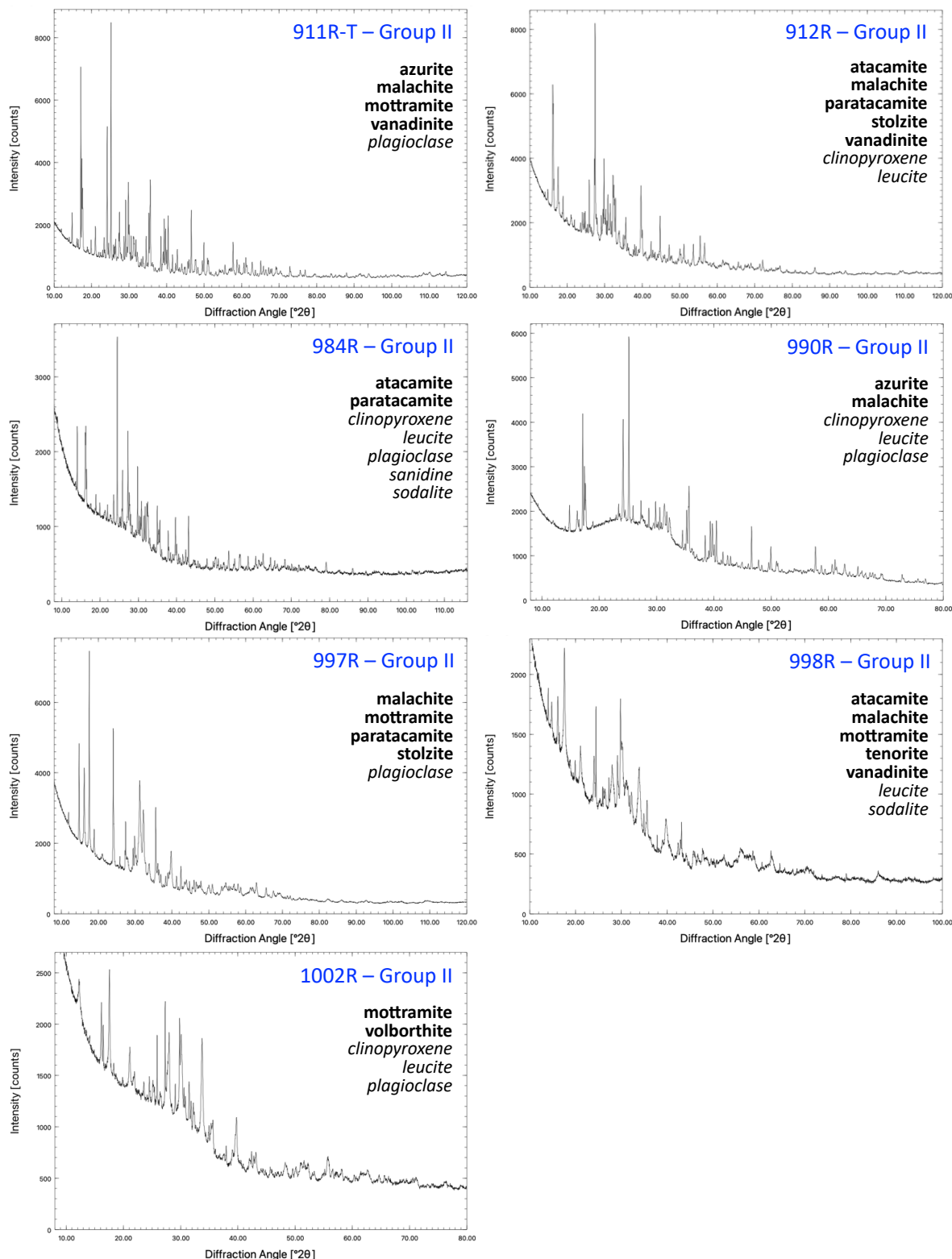


FIGURE S1. XRPD patterns of the investigated samples of Groups I and II, with the indication of the main recorded phases (sublimate minerals in bold, minerals from the lava host rock in *italics*).

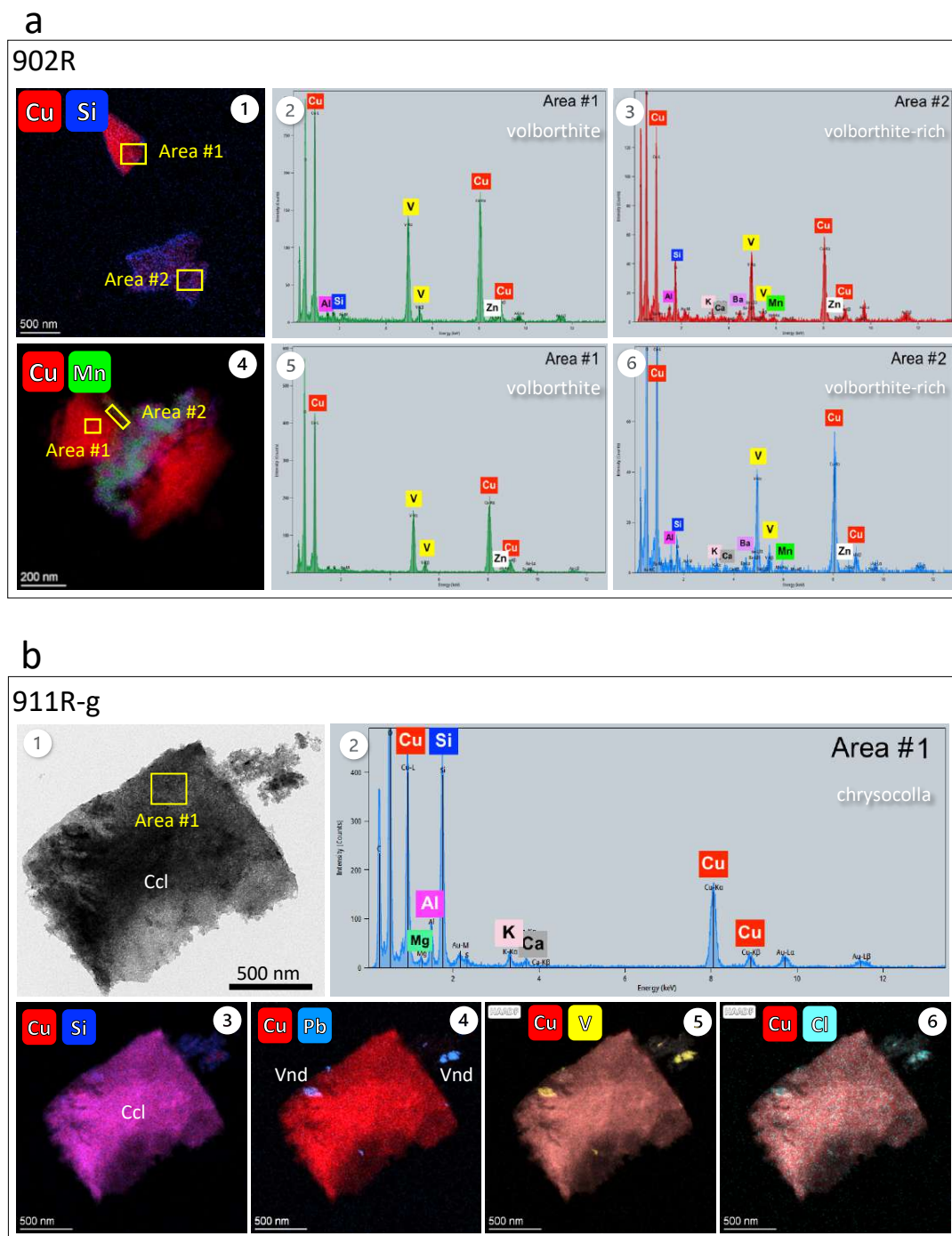
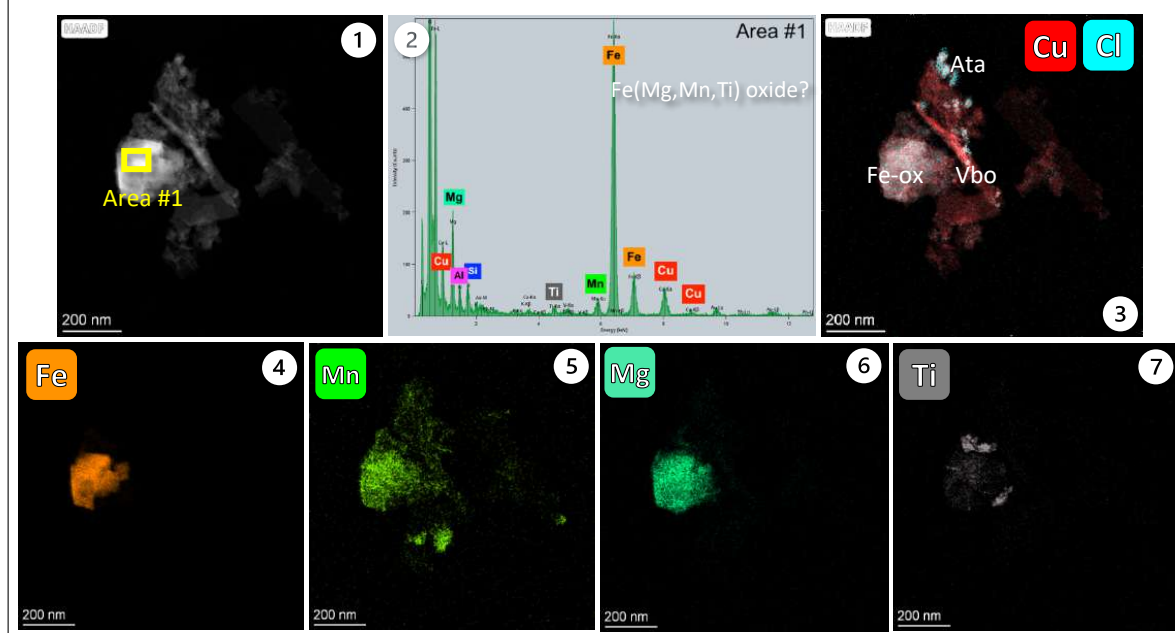


FIGURE S2. TEM-HRTEM-SAED-EDS data of samples of Group I. **(a)** 902R. Volborthite grains and mixed particles; 1. Cu-Si chemical map of volborthite and volborthite-rich fragments; 2. EDS spectrum of volborthite (Area #1 in 1), with trace amounts of Zn, Si and Al; 3. EDS spectrum of a supposed mixed volborthite-silicate-oxide particle (Area #2 in 1), having small contents of Si, Al, Ca and K, as well as Mn, Ba and Zn; 4. Cu-Mn chemical map of a heterogeneous particle; 5. EDS spectrum of volborthite (Area #1 in 4), with trace content of Zn; 6. EDS spectrum of Area #2 in 4, referring to the greenish-colored areas, and showing small amounts of Mn, together with Si, Al, Ca, K, Ba and Zn (mixed volborthite-silicate-oxide?). **(b)** and 911R-g. Chrysocolla-rich grain; 1. textural image, with darker areas and rounded structures (lower part); 2. EDS spectrum of Area #1 in 1, attributable to chrysocolla; 3.–6. chemical maps of the fragment in 1, with the distribution of Cu-Si, Cu-Pb, Cu-V and Cu-Cl, respectively. Symbols as in Table 2.

a

P9



b

P9

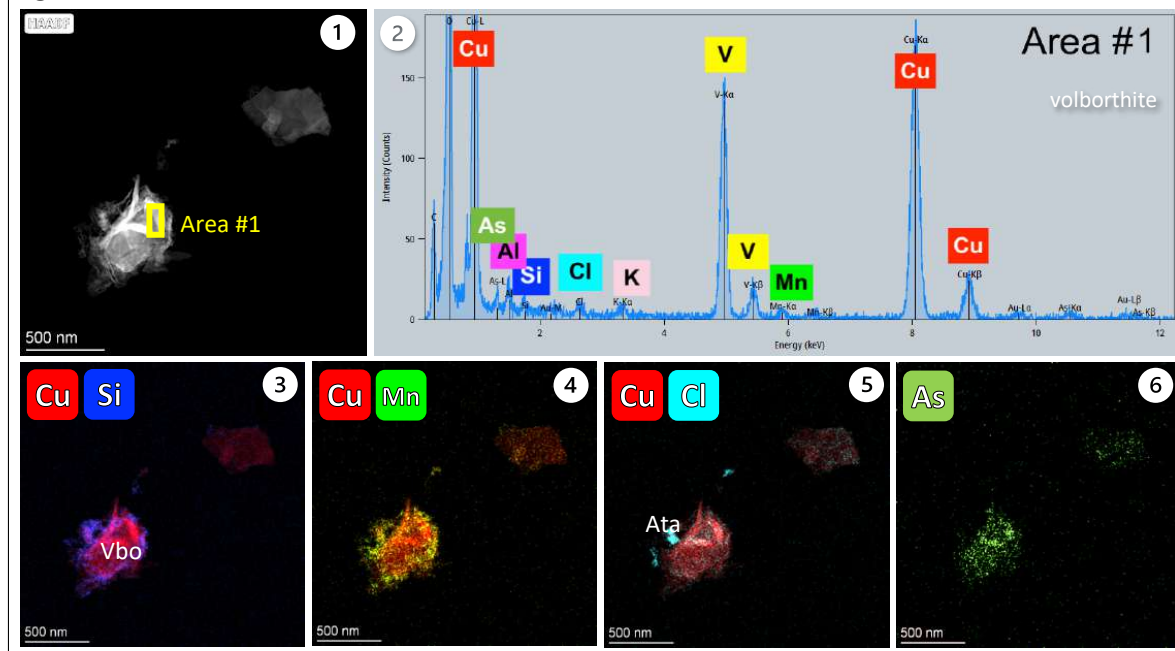


FIGURE S3.—Continued on next page.

C

P9

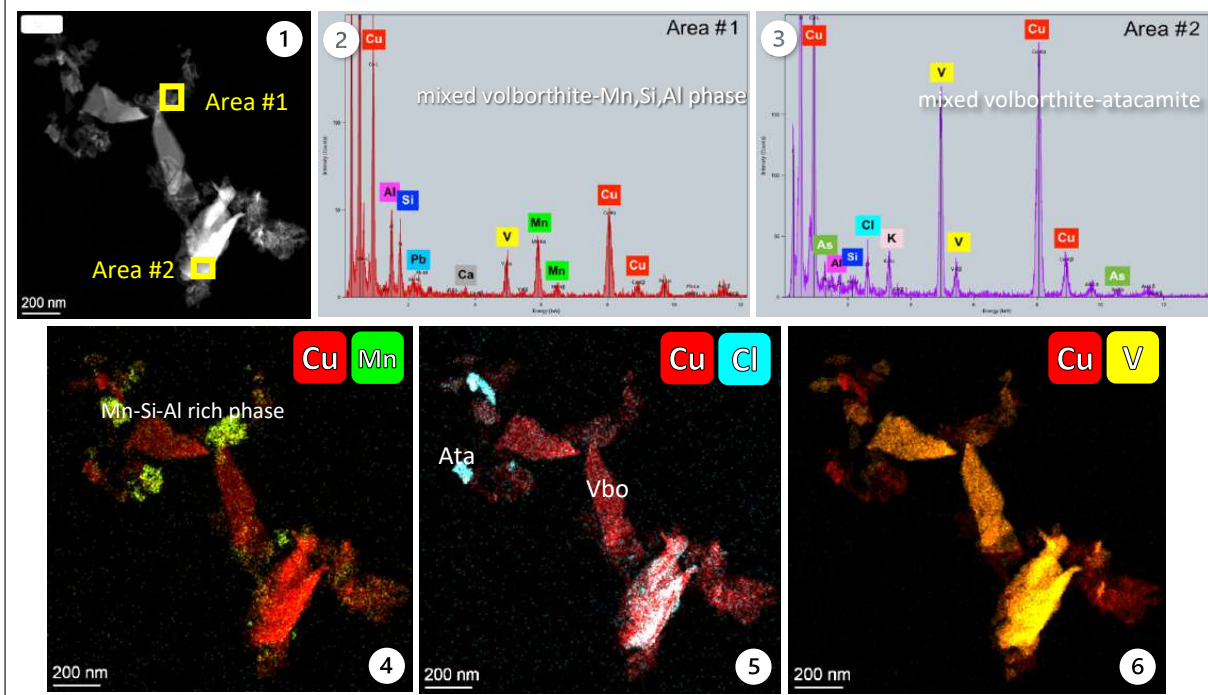


FIGURE S3. TEM-HRTEM-SAED-EDS data of sample P9 (Group II). (a) Mixtures of volborthite, atacamite and a likely Fe oxide; 1. HAADF image; 2. EDS spectrum of Area #1 in 1, corresponding to a possible Fe(Mn,Mg,Ti) oxide with minor amounts of Cu from the surrounding particles; 3.–7. chemical maps of Cu-Cl, Fe, Mn, Mg(+Ti), respectively. (b) Volborthite-prevailing fragments; 1. HAADF image; 2. EDS spectrum of Area #1 in 1; 3.–6. chemical maps of Cu-Si, Cu-Mn, Cu-Cl and As, respectively. (c) Mixed grains; 1. HAADF image; 2.–3. EDS spectra of Areas #1 and #2 in 1, respectively; 4.–6. chemical maps of Cu-Mn, Cu-Cl, and Cu-V, respectively. Symbols as in Table 2.

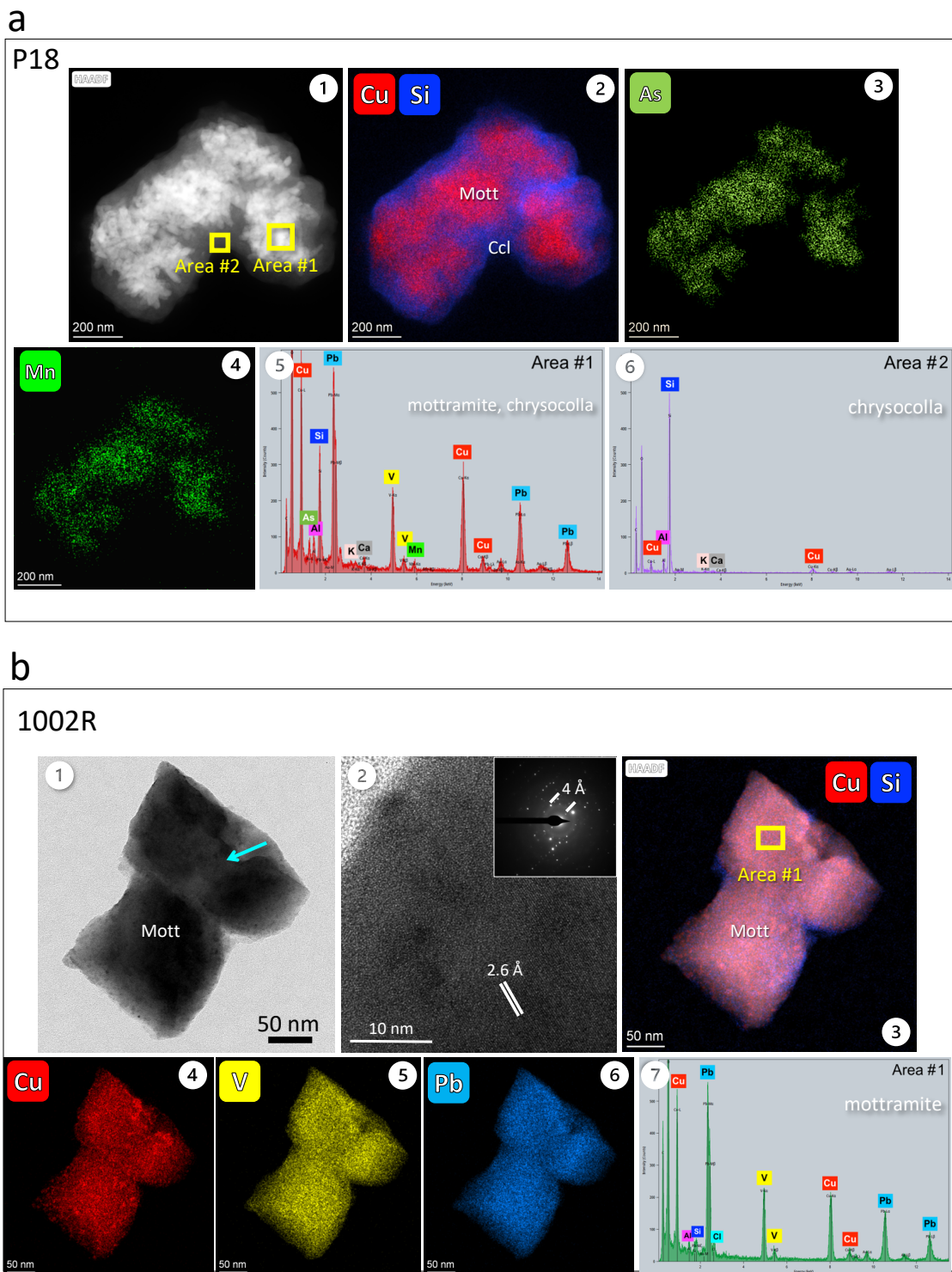


FIGURE S4. TEM-HRTEM-SAED-EDS data of samples P18 and 1002R (Group II). (a) P18. Mixed mottramite-chrysocolla grain; 1. textural image (HAADF) displaying aggregates of euhedral mottramite crystals surrounded by chrysocolla; 2. 3. 4. chemical maps of the particle in 1, showing the distribution of Cu-Si, As and Mn; 5. EDS spectrum of a mixture of mottramite and chrysocolla (Area #1 in 1); 6. EDS spectrum of chrysocolla (Area #2 in 1). Symbols as in Table 2. (b) 1002R. Mottramite aggregate; 1. textural image; 2. lattice fringe image of mottramite (referring to the area indicated by the sky-blue arrow in 1), with corresponding to 2.7 Å spacing (212), and the related SAED pattern in the inset (4.0 Å, (102); 3. HAADF chemical map with Cu-Pb distribution; 4. 5. 6. chemical map of Cu, V and Pb of mottramite, respectively; 7. EDS spectrum of mottramite (Area #1 in 3). Symbols as in Table 2.

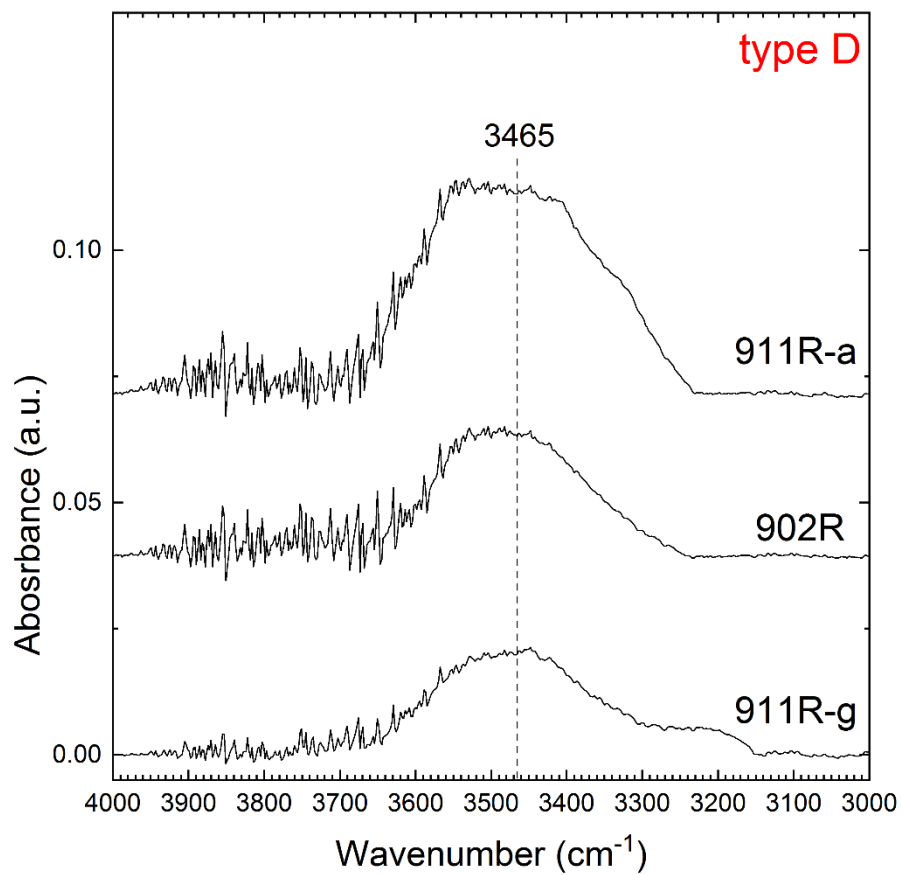


FIGURE S5. OH spectra of Type D (see text for description).