



**Figure S4.** Scatter plots documenting the main ion substitution mechanisms involved in wolframite besides the usual  $\text{Fe}^{2+} = \text{Mn}^{2+}$  interchange (a), and accounting for the incorporation of  $\text{R}^{3+}$  (mostly  $\text{Fe}^{3+}$ , but also sporadic Cr and V),  $\text{R}^{5+}$  ( $\text{Nb} \gg \text{Ta}$ ) and  $\text{R}^{4+}$  ( $\text{Zr} > \text{Ti} \gg \text{Si}$ ) ions in sites ideally occupied by ( $\text{Fe}^{2+}$ , Mn) and W (b, c). Cross-plots (d) and (e) show the irregular enrichments of (Nb + Ta) and (Zr + Ti + Si) displayed by *Wolf I* and *Wolf II*. In all plots, apfu = atoms per formula unit.