



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 R^{3+} (mostly Fe^{3+} , but also sporadic Cr and V), R^{5+} ($\text{Nb} \gg \text{Ta}$) and R^{4+} ($\text{Zr} > \text{Ti} \gg \text{Si}$) ions in sites ideally occupied by $(\text{Fe}^{2+}, \text{Mn})$ and W (b, c). Cross-plots (d) and (e) show the irregular enrichments of $(\text{Nb} + \text{Ta})$ and $(\text{Zr} + \text{Ti} + \text{Si})$ displayed by *Wolf I* and *Wolf II*. In all plots, apfu = atoms per formula unit.