Mineral wool products can be used for thermal and acoustic insulation as well as for fire protection. The high temperature properties and the crystallization behaviour (devitrification) of the amorphous fibres during heating have been examined. Commercial stone wool and commercial hybrid wool (stone wool produced by a glass wool process) have been compared, as well as specially produced stone wool fibres. The fibres differed in chemical compositions and degree of oxidation given by Fe\textsuperscript{3+}/Fe\textsubscript{total} ratios. The materials were studied by thermal stability tests, X-ray diffraction, Mössbauer spectroscopy, secondary neutral mass spectroscopy, differential scanning calorimetry and thermal gravimetric analysis. When stone wool fibres were heated at 800 °C in air, oxidation of Fe\textsuperscript{2+} to Fe\textsuperscript{3+} occurred simultaneously with migration of divalent cations (especially Mg\textsuperscript{2+}) to the surface. Decreasing Fe\textsuperscript{3+}/Fe\textsubscript{total} ratios resulted in increasing migration and improved thermal stability. The cations formed a surface layer mainly consisting of MgO. When heated to above 800 °C, bulk crystallization of the fibres took place with diopside and nepheline as the main crystalline phases. Commercial stone wool and the specially made fibres were considerably more temperature stable than the commercial hybrid wool. Commercial hybrid wool has a high Fe\textsuperscript{3+}/Fe\textsubscript{total} ratio of 65% resulting in less migration of cations during heat treatment.