For decades, archaeologists have used a number of techniques to determine the compositions of geological sources of chemically homogenous materials and then attempted to match artifacts to sources to understand trade and exchange of material objects. Such provenance research is common with glassy rhyolites (obsidian) that were used wherever available as a source of raw material for flaked stone artifacts such as projectile points and cutting tools. Portable X-ray fluorescence (PXRF), of all of the analytical techniques available for obsidian compositional analysis, has the potential to make the greatest impact by combining non-destructive analysis with rapid results, relatively low equipment and analysis cost, and the option of in-field analysis. While PXRF is a powerful research tool, its successful use in obsidian provenance research requires an understanding of X-ray physics, igneous petrology, the calibration process, and the ability to test a sufficient variety of homogeneous and well-characterized reference materials suitable for developing a valid calibration curve. The potential for “point and shoot” PXRF is hampered in part by the all of these factors.