A rapidly growing suite of spectroscopic tools has enabled significant advances in our understanding of short-range structure in glasses. Among these, NMR spectroscopy has been developed to the point where it is routine to identify and quantify different types of network-forming polyhedra, at least for those isotopes possessing favorable NMR properties (e.g. 11B, 27Al, 31P etc...). When used to develop structural models for different glass systems as a function of composition, NMR data on cation speciation is invaluable. Recent work on topological constraint theory in glasses has resulted in more demand for such structural data and models. Atoms in network glasses are constrained by their chemical bonds and bond angles, and the strengths of these constraints depend on the local topology and the chemical nature of the elements. NMR spectroscopic studies of the short-range network structure reveal the identity of these constraints, thus enabling development of a quantitative structural model for borophosphate and phosphosilicate glasses. This combination of detailed structural understanding and topological constraint theory can explain the mixed network former effect (MNFE) in these types of systems, and gives accurate predictions for the composition dependence of glass transition temperature, liquid fragility and indentation hardness.