A. PROJECT SUMMARY

Framework structures encompass a wide range of natural and synthetic compounds of importance in the Earth sciences, solid state chemistry, condensed matter physics, and materials sciences. Framework structures are materials whose atomic structure can be described in terms of the linking together of tightly-bonded groups of atoms such as SiO_4 or PO_4 that can be thought of forming relatively rigid polyhedra whose corners are formed by the anions such as oxygen. The frameworks are then formed by the condensation of these polyhedra, i.e. by sharing of the oxygen anions. Examples of framework structures formed of tetrahedral groups such as SiO_4 and AlO_4 include major groups of minerals such as the feldspars (60% of the Earths crust), and zeolites that are the most important family of catalysts in the chemical industry. Other frameworks, including minerals stable in the deeper Earth such as garnets, incorporate network-forming tetrahedra and octahedra. Perovskites, which are probably the single most technologically-important group of compounds because of their electrical and elastic properties, are examples of frameworks composed entirely of corner-linked octahedra.

Understanding the principles of behavior of these common structure types is important for a number of reasons. For example, in geochemistry we need to be able to predict the limit of solid solution of other components into end-member compounds. For geophysics one needs to predict the influence of these minor chemical components on the elasticity of minerals. The interaction of elastic and structural properties is also important for understanding the behavior of such perovskites such as ferro-relaxors and ferro-elastics that are used in many industrial devices. High-pressure studies can provide important insights into the general properties of frameworks for several reasons. First, pressure is energetically a far stronger driving force than temperature and thus one can explore a far greater range in structural behavior by compressing a structure rather than heating it. Second, pressure allows the repulsive regime of the inter-atomic potential to be explored directly. And, third, determination of the unit-cell constants of a material yield not only the volume as a function of pressure (for thermodynamic calculations and petrology) and the bulk modulus which is important for geophysical interpretations, but also certain combinations of individual elastic moduli. The philosophy of the research that we propose to undertake is to study the evolution of selected structure types under pressure by single-crystal X-ray diffraction up to pressures of 10 GPa. Current methodologies do not allow the sufficiently precise determination of the structural parameters of crystals under high pressures to identify all of the small changes that occur in framework structures as pressure is applied. Therefore a significant part of the work proposed in this grant is devoted to the improvement in the experimental techniques, which we expect will have wider applications than to high-pressure research alone. From the specific results we expect to be able to derive general principles concerning the behavior of framework structures under a range of conditions.