The selection of polymorphic metal oxides as candidate materials for applications in heterogeneous catalysis depends strongly on the accurate prediction of polymorph phase stability under particular synthesis reaction conditions. By changing the reaction conditions under which polymorphic materials are synthesized, the relative energetic stabilities of polymorph structures can be altered, causing metastable material phases to become thermodynamically stable. In cases where metastable phases are energetically similar to stable phases, experimental procedures such as epitaxial thin film stabilization or moderately changing synthesis temperature can be employed to access these phases without the costly application of high pressure. When subjected to high temperatures or pressures in compression and decompression experimental procedures, metastable phases within energetic windows of epitaxial stabilization can observe phase transitions that differ from those observed by stable phases either thermodynamically or kinetically.

Prediction of phase stability and transition pressures is particularly important in the context of photocatalysis, as the anatase polymorph of TiO_2 is the most reactive active catalytic material of commonly studied TiO_2 polymorphs that exists at ambient pressure in most experimental setups. However, TiO_2 polymorphs that are accessible only at higher pressures, such as α-PbO_2 and fluorite, can be suitable active photocatalyst candidates in mixed-metal oxides, while polymorphs that are accessible under different synthesis procedures performed at ambient conditions, such as rutile and brookite, can serve as supports for metal catalysts that determine metal surface orientation. In the case of a single polymorph composition placed under limited reaction conditions, phase transitions can be affordably characterized by solely experimental research, leading to the discovery of the least costly conditions under which desired high pressure polymorphs can be synthesized. However, when considering a large set of BO_2 polymorph compositions (B = Ti, V, Ru, and Ir) over a wide range of temperature and pressure conditions, the experimental discovery of all possible pressure-induced phase transitions for the stabilized phases of these BO_2 is intractable. Thus, a first-principles methodology capable of accurately and efficiently predicting the reaction condition dependent relative energetic stabilities of and phase transition pressures between polymorphic materials must be developed. Given that the energetics of 3*d* metal containing oxides can be computed inaccurately by standard DFT GGA functionals, the DFT+U method and self-consistent implementation of the linear response method for determining Hubbard U values are employed.

In this work, the effects of incrementally changing the U value on the 3*d* orbitals of Ti cations in TiO_2 polymorphs is initially inspected, revealing that the prediction of relative energetic stability ordering of the Rutile, Anatase, and Columbite polymorphs is consistent with experiment in the approximate range U = 2.8 – 4.2 eV. Previous first principles studies have resolved self-consistent linear response U values for the Rutile and Anatase polymorph Ti cations of 3.23 and 3.25 eV, respectively. Applying the average of these two theoretically calculated U values to the Rutile, Anatase, and Columbite polymorphs successfully predicts their experimentally observed energetic stability ordering. Imposing a U parameter of 3.24 eV on these three polymorphs also leads to the almost exact prediction of two of the three phase transition pressures involving them, namely the ambient pressure transition from Anatase to Rutile and the transition from Rutile to Columbite at 10.0 GPa. The transition from Anatase to Columbite, which occurs at 2.6 GPa in experiment, is moderately underestimated by first principles calculations at 1.4 GPa. Given the reproducibility of experimental results in bulk TiO_2 polymorphs, relative energetic stability and phase transition calculations are applied to bulk VO_2, RuO_2, and IrO_2 polymorph sets, while calculations are repeated on these polymorph sets using different

pseudopotentials to ensure that predictions are not significantly affected by pseudopotential selection. Additional Hubbard U values applied to the resolution of energetic results calculated via self-consistent linear response theory are performed for comparative purposes.