The carbon cycle fundamentally depends on the precipitation of carbonate minerals, such as aragonite, calcite, and dolomite. Carbonate minerals form the skeleton and shells of organisms, and by removing carbon from the atmosphere, they influence climate change occurring over geological timescales. They similarly underlie carbon capture sequestration (CCS) strategies for mitigating climate change occurring on shorter, human timescales. Carbonate minerals also contain other elements, such as calcium (Ca) and strontium (Sr). Because Ca and Sr naturally occur as different isotopes, understanding how Ca and Sr isotopes behave during carbonate precipitation can shed light on the rates and mechanisms of carbonate precipitation. Recent innovations in mass-spectrometry now permit precise analysis of mass-dependent fractionation (separation) of Ca and Sr isotopes. To this end, we proposed to quantify if, how, and to what extent Ca and Sr isotopes fractionate during carbonate mineral precipitation. The ultimate aim of the project is to develop novel methods for testing the efficacy of CCS strategies involving forced precipitation of carbonate minerals in the shallow subsurface.

Previous research has shown that carbonate mineral precipitation can fractionate Ca isotopes, but the mechanisms are not well understood. Possibilities include kinetic fractionation during diffusion [1], precipitation rate effects [2], equilibrium isotope partitioning [2,3], adsorption processes [4], and surface entrapment [5,6]. Undoubtedly, analogous mechanisms fractionate Sr isotopes, but no studies have addressed these issues. While the surface entrapment model seems to provide the best explanation for fractionation of Ca isotopes, limited control of precipitation rates has hampered unambiguous interpretation of the results. For example, Lemarchand et al. (2004) proposed that calcite precipitation elicits a relatively large equilibrium isotope effect, but subsequent researchers [e.g., 4,6,7] have argued that the fractionation more likely reflects a kinetic isotope effect stemming from the rapid precipitation of calcite in Lemarchand et al.’s (2004) homogeneous nucleation experiments. Tang et al. (2008) used a membrane-diffusion method to homogeneously nucleate calcite, but precipitation rates changed throughout their experiments. In general, homogeneous nucleation of calcite and heterogeneous growth of calcite on a pre-existing surface proceed by fundamentally different mechanisms likely having characteristic isotope effects.

The chemostat method overcomes these and other limitations because it maintains constant precipitation rates during carbonate formation, and the introduction of seed material into a metastable solution causes heterogeneous growth of a mineralogically pure solid on a pre-existing template [8]. The chemostat method also allows precise control over other key parameters governing carbonate precipitation, namely pCO₂, pH, and temperature. Mineralogical effects are easily investigated by employing the appropriate seed material. We hypothesized that the superior experimental control offered by the chemostat method would help elucidate the controlling mechanisms of Ca and Sr isotope fractionation, thereby permitting improved understanding of carbonate mineral precipitation in nature.

We directed ISEN finding to build a chemostat. Figure 1 provides a schematic of the chemostat. The chemostat method works by mixing varying concentrations of cation (CaCl₂ or
equilibrated with pure CO$_2$ gas in a water-jacketed (temperature controlled) reaction vessel. Experimental pCO$_2$ and pH values are adjusted and maintained by bubbling CO$_2$/N$_2$ gas mixtures through the reaction vessel solution. The solution pH increases to a state of supersaturation below that for homogeneous nucleation but above that for heterogeneous precipitation. At this point, addition of seed material causes heterogeneous carbonate growth. Computer software monitors pH and utilizes peristaltic pumps to add either cation or anion solution to balance small changes in chemistry during mineral formation. These feedbacks maintain constant precipitation rates at fixed solution composition. Once sufficient overgrowth has precipitated, usually within 24 to 48 hours, the experiment is terminated and the solid is separated by filtration.

So far, we have used the chemostat to investigate fractionation of Ca isotopes during precipitation of calcite at a temperature of 25°C and a pCO$_2$ of 390 µatm. We analyzed the Ca isotope composition of crystals and solutions using a novel TIMS method recently developed at Northwestern University [9]. Initial data are plotted in Figure 2. The data show that calcite overgrowths preferentially incorporate $^{40}$Ca over $^{44}$Ca and that the degree of isotopic discrimination positively correlates with precipitation rate. In other words, the degree of isotopic fractionation increases as precipitation rates increase. The calcite crystal lattice is less selective at slower precipitation rates. Work is ongoing to numerical model the data and to investigate other experimental conditions.