Recently, we introduced a novel molecular simulation method (denoted as “harmonically mapped averaging”) to efficiently average molecular simulation samples for crystalline systems, yielding orders of magnitude CPU speedup compared to conventional methods. We now report the results of calculations to determine the crystal structures of iron at extreme temperatures and pressures, typical of those found in the Earth’s inner core. We obtain values of the free energy over relevant state conditions using high-quality first-principles methods, yielding results of unprecedented accuracy and precision. In particular, we assess the relative phase stability of all candidate structures (fcc/hcp/bcc) over pressures from 150 to 500 GPa and temperatures from 4000 to 7000 K. This knowledge should be a key ingredient in the longstanding debate about the actual crystal structure of the Earth’s inner core. Furthermore, this study demonstrates that first-principles molecular simulation can be a crucial tool for the field of mineral physics, and in particular toward understanding and characterizing the deep interior of the Earth and other planets, which exhibit conditions that are not reliably measurable by experiment. The methods demonstrated in this work should help to position molecular simulation as an alternative source of data for well-defined crystalline systems, data that are as or more accurate than can be obtained by experiment.