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First-principles study of sulfur isotope fractionation in pyrite-type disulfides

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Abstract

The sulfides are an important group of minerals. As a geochemical tracer, the sulfur isotope fractionation in sulfides can be used to analyze the ore-forming process and the ore-forming material source. Fe, Co, Ni, and Mn are the first row transition metals, and pyrite (FeS_2), cattierite (CoS_2), vaesite (NiS_2), and hauerite (MnS_2) crystallize in the pyrite-type structure. However, there are few studies on the sulfur isotope fractionation in these disulfides. So studying the isotope fractionation between them provides the opportunity to examine the various members of a structural group in which only the metal atom is changed, thereby providing information that permits a systematic development of concepts regarding sulfur isotope fractionation in transition-metal disulfides. In the present paper, the sulfur isotope fractionation parameters for pyrite, cattierite, vaesite, and hauerite with the pyrite-type structure have been calculated using first-principles methods based on density functional theory in the temperature range of 0–1000 °C. The structure parameters of these four minerals and the vibration frequencies of pyrite are in good agreement with previous experimental values. The metal-sulfur distance increases in the order FeS_2, CoS_2, NiS_2, and MnS_2, the sulfur-sulfur distance decreases in the order FeS_2, CoS_2, MnS_2, and NiS_2, these two sequences agree with the experimental results. Our calculations show that the order of heavy isotope enrichment is pyrite > cattierite > vaesite > hauerite. It seems that the sulfur isotope fractionation in disulfides depends mainly on the metal-sulfur bonds.

Keywords: Sulfur isotope fractionations, disulfides, pyrite, first-principles, DFPT