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Germanium/silicon differentiation at hydrothermal conditions: An ab initio molecular dynamics study

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Gaining insight into the distribution of rare but critical metals at the atomic level is a scientifically important, yet technically challenging aspect of comprehending ore formation and exploration. Germanium is one such economically critical metal that resembles silicon (Si) from a geochemical perspective due to their similar ionic radii and electron configurations, as both elements are in the IVA group of the periodic table. Consequently, in the crustal environment, Ge tends to mimic the geochemical behaviors of Si and even substitute Si in the lattice sites of minerals. Since silicon is evenly distributed throughout the Earth's crust, germanium follows this pattern and so, we rarely observe a Ge deposit, although its crustal concentration is 1.5 ppm, similar to that of W, Mo, and Sn with relatively extensive ore deposits. However, there are a few exceptions, such as coal and zinc deposits, where the concentration of Ge is high enough for economical extraction. Moreover, it is now known that Ge is more abundant in epigenetic sedimentary-hosted Zn deposits compared to other high-temperature Zn deposit types.

Previous experimental works suggested that under the geochemical conditions relevant to ore genesis, $Ge(OH)_4$ and $Si(OH)_4$ are the most abundant species for Ge and Si in the aqueous phase; however, complexation with F^- and S^{2-} is also expected, where the affinity for those elements is high. In this regard, we explored the differentiation of Ge from Si utilizing thermodynamic integration based on ab initio molecular dynamics simulation at a supercritical condition (673 K) similar to a hydrothermal solution with a magmatic origin and a subcritical temperature (423 K) similar to an epigenetic condition.

Our findings indicate that silicon is preferentially enriched in the aqueous phase, while germanium is found in the gas phase. Furthermore, the calculated free energies of the reactions at those temperatures suggest that the Si/Ge differentiation is more pronounced at lower temperatures. This aligns with field observations indicating that germanium is enriched in low-temperature deposits, such as coal mines and epigenetic zinc deposits.