Speciation analysis of Fe in single plagioclase crystals separated from two different gabbros was performed to understand the crystallization mechanisms of magnetite exsolution. Iron species in single crystals were measured using Fe K- and L_{III}-edge X-ray absorption fine structure (XAFS) analysis. The K-edge pre-edge analysis showed variation in the averaged valence state of Fe in plagioclase crystals even if they had been separated from the same gabbro that was further confirmed by the L_{III}-edge analysis. The K-edge pre-edge analysis also suggests the various degrees of contribution from tetrahedral Fe. The mixing of tetrahedral and octahedral Fe leads to an underestimation of the averaged valence state of Fe for the K-edge pre-edge analysis; thus, we adopted the L_{III}-edge result for the valence state of Fe in plagioclase crystals. Iron K-edge extended XAFS (EXAFS) analysis of two plagioclase crystals separated from the same gabbro clearly showed different coordination environments. A weakening of EXAFS oscillation was recognized in one sample, because two Fe‒O bonds (Fe^{3+}‒O_1 and Fe^{2+}‒O_2) cancelled out the oscillations of each other. The EXAFS spectrum of the other plagioclase crystal suggested a homogeneous distribution of Fe. The content of exsolved magnetite in these crystals is nearly identical, indicating that the exsolution of magnetite in plagioclase crystal had been completed before the temperature decrease that stopped the ordering of Fe ions in tetrahedral sites.