Oxide Production Mechanism in LA-ICPMS Revealed by Comprehensive Analysis of REE-Th-U Phosphates

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Oxide production in laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) can cause spectral interferences precluding accurate determination of trace element abundances and isotopic ratios in geological samples. Previous studies revealed that the oxide production depends on many analytical parameters such as sample gas flow rate, plasma power and cone geometry. However, the understanding of what processes control the oxide production within ICP-MS is not enough. We investigated the mechanism of oxide production within ICP-MS by comprehensive analysis of synthetic and natural phosphates. Oxide production rates (MO^+/M^+) of 16 rare earth elements (REE), Th and U were determined at various sample gas flow rates. The response of MO^+/M^+ to gas flow change was quite different among the REE, depending on the oxide bond energy. The MO^+/M^+ of elements with low oxide bond energies were nearly constant over the range of studied sample gas flow rates, whereas those with high oxide bond energies increased with the gas flow rate from 0.85 to 1.00 L min^{-1}. Furthermore, the latter showed a linear correlation between Log (MO^+/M^+) and oxide bond energy where the slope is steeper at a higher gas flow rate. This linear correlation suggests that an equilibrium reaction between MO^+ and M^+ + O within the plasma controls the observed MO^+/M^+ for strong-oxide forming elements, in which the steeper slope reflects a lower equilibrium temperature. This equilibrium reaction also explains the increase of MO^+ signals with the concomitant decrease of M^+ signals observed for these elements. In contrast, the independence of MO^+/M^+ on the gas flow rate observed for weak-oxide forming elements indicates that reactions within the boundary layer and/or interface region of ICPMS would rather control the MO^+/M^+. We found that the observed relation between Log(MO^+/M^+) and oxide bond energies can be well explained by oxide formation through collision of M^+ and metastable O followed by radiative decay of excited MO^+ to the ground state in the interface region. Our results demonstrate that the relative significance of these two independent oxide production processes change among the elements depending on the oxide bond energy and on analytical conditions controlling the plasma temperature.

Keywords: rare earth element, monazite, laser ablation, ICP-MS

