Goldschmidt 2023 Abstract
https://doi.org/10.7185/gold2023.17384

The oxidation state of titanium in reduced extraterrestrial melts

ANDREW BERRY[1], PATRICIA DOYLE[2], PAUL SCHOFIELD[3], LAURA MILLER[1], CHARLES LE LOSQ[4], ANTONY BURNHAM[1] AND J. FREDERICK W. MOSSELMANS[5]

[1]Australian National University
[2]Imperial College London
[3]Natural History Museum
[4]Université Paris Cité, IPGP
[5]Diamond Light Source

Presenting Author: andrew.berry@anu.edu.au

Titanium occurs exclusively as Ti^{4+} in most natural terrestrial materials, however, under reduced conditions it may also occur as Ti^{3+}. For example, Ti^{3+} is found in armalcolite in high-Ti Lunar basalts and in both hibonite and fassaite in chondritic meteorites. The proportion of Ti as Ti^{3+} in these minerals is a potential indicator of the oxygen fugacity (fO_2) of the process during which they formed. However, predicting Ti^{3+}/Ti^{4+} in the system from which these minerals may have crystallised is experimentally challenging because of the extremely reduced conditions.

The oxidation states of Ti in five synthetic silicate glass compositions, quenched from melts equilibrated at 1400 ˚C, atmospheric pressure, and fO_2s in log units relative to the fayalite-magnetite-quartz (FMQ) buffer from FMQ+3.3 to FMQ-10.2 (from +6.6 to -6.9 log units relative to iron-wüstite, IW), were investigated by Ti K-edge X-ray absorption near edge structure (XANES) spectroscopy. All spectra could be well fit by a linear combination of the spectra recorded from the most oxidised and reduced samples of the same composition, indicating that the samples only contain two Ti species. Ti^{3+}/Ti_{Tot} (where $Ti_{Tot} = Ti^{3+} + Ti^{4+}$) = 0 for the most oxidised samples but is unknown for the most reduced. Thus, the linear combination fit results were used in a regression model in which Ti^{3+}/Ti_{Tot} of the reduced end-member was varied to give Ti^{3+}/Ti_{Tot} values of the other samples that best fit the thermodynamically expected dependence of Ti^{3+}/Ti_{Tot} on fO_2. The most reduced samples were found to have Ti^{3+}/Ti_{Tot} ~ 0.6. The resulting modified equilibrium constants of the Ti oxidation reaction, logK', are linearly correlated with the optical basicity parameterisation of melt composition, such that as optical basicity decreases, Ti^{3+}/Ti_{Tot} increases, at constant fO_2. This correlation allows Ti^{3+}/Ti_{Tot} to be predicted for other compositions and, assuming that the temperature dependence of Ti^{3+}/Ti^{4+} is parallel to FMQ, a general equation relating Ti^{3+}/Ti^{4+} to fO_2 was obtained. This equation was used to predict Ti^{3+}/Ti_{Tot} as a function of fO_2 for high-Ti Mare basalt, chondrule (CV and CM), and calcium aluminium inclusion (CAI; Type A and B) compositions.