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Hydrogen deficiency in Ti-rich biotite from anatectic metapelites (El Joyazo, SE Spain): Crystal-chemical aspects and implications for high-temperature petrogenesis

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ABSTRACT

Titanium-rich biotites from graphite-bearing metapelitic xenoliths, equilibrated at ca. 850 °C and 7 kbar in the presence of a granitic melt, have been studied through complete chemical analysis and single-crystal XRD refinements. The chemical study combines EMP analyses, hydrogen determination by both SIMS and C-H-N elemental analysis, and Mössbauer spectroscopy. Biotites in the analyzed xenoliths have TiO_2 contents ranging from 4.5 to 4.9 wt% and an X_{Fe} of 0.67. Their F and Cl contents are negligible, and Fe^{3+}/Fe_{tot} ranges from 10 to 16%. The H_2O content of the biotites ranges from 2.4 to 2.8 wt%, and a small fraction of H is accommodated in the lattice as NH_4. Based on these full chemical analyses, the calculated OH occupancy is 1.26 to 1.30 groups per formula unit, more than one third less than the stoichiometric value.

The entrance of Ti in the octahedral site of biotite is consistent with the Ti-oxy exchange, whereas Ti-Tschermak or Ti-vacancy substitutions play a very minor role. The Fe^{3+}-oxy exchange cannot account for the observed OH deficiency.

From single-crystal XRD, biotites belong to the 1*M* polytype and contain variable amounts of stacking faults. The *c* cell parameter, K-O4 and $\langle K\text{-}O\rangle_{outer}$ distances provide an independent estimate of the OH content, which agrees with SIMS determinations. The linear relationship between $^{VI}Ti^{4+}$ and the bond-length distortion of the *cis*-M2 octahedron reveals the partitioning of Ti^{4+} in M2, and the Ti^{4+} off-center shift toward O4 supports the occurrence of the Ti-oxy exchange. The ordering of Ti^{4+} over two non-equivalent M2 sites, which would be favored energetically, is in agreement with the evidence for a third octahedral site suggested by Mössbauer spectroscopy. The biotite dehydrogenation combined with the partitioning of Ti^{4+} in M2 and the low thermal expansion of Ti^{4+}-containing octahedra, are the keys to understanding the thermal stabilization of Ti substitution in biotites.