Mineral chemistry of Ti-rich biotite from pegmatite and metapelitic granulites of the Kerala Khondalite Belt (southeast India): Petrology and further insight into titanium substitutions

BERNARDO CESARE,1,2,* MADHUSOODHAN SATISH-KUMAR,3 GIUSEPPE CRUCIANI,4 SHABEER POCKER,3 AND LUCA NODARI5

1Dipartimento di Geoscienze, Università di Padova, Via Giotto 1, Padova, 35137, Italy
2C.N.R., Istituto di Geoscienze e Georisorse, Sezione di Padova, Corso Garibaldi 37, Padova, 35137, Italy
3Institute of Geosciences, Shizuoka University, Oya 836, Shizuoka, 422-8529, Japan
4Dipartimento di Scienze della Terra, Università di Ferrara, Via Saragat 1, Ferrara, 44100, Italy
5Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo 1, Padova, 35131, Italy

ABSTRACT

Precise chemical composition, including Fe3+ and H, of biotite from a pegmatite dike and its host granulite from the Kerala Khondalite Belt of SE India has been determined using a multi-technique approach involving EMP, SIMS, Mössbauer, and C-H-N elemental analysis. Biotite in these rocks formed at T > 800–850 °C and P = 5 ± 1 kbar.

The full analyses were normalized on the basis of [O12–(x+y+z)(OH)xClyFz]. Biotite in the pegmatite is Ti-, F-, and Cl-rich (0.33, 0.46, and 0.16 apfu, respectively), H2O-poor (OH = 0.86 pfu), has XMg = 0.49 and Fe3+/Fe tot ≤ 3%. The low octahedral vacancies (0.06 pfu) and the high oxygen content in the hydroxyl site (OH + F + Cl = 1.49 pfu) confirm the role of the Ti-oxy substitution as a major exchange vector in these high-T biotites.

In the host granulite, fine-grained biotite is Fe3+-free, has low Cl (0.03 apfu), and more variable composition, with Ti, F, and XMg in the ranges 0.26–0.36, 0.52–0.67, and 0.67–0.77, respectively. The number of octahedral vacancies is relatively large (0.10–0.18 pfu) and the sum of volatiles (OH + F + Cl) varies from 1.71 to 2.06 pfu. Systematic variations of XMg are a function of the microstructural position and are in agreement with retrograde exchange reactions: biotite included in or in contact with garnet has the maximum values, whereas crystals in the matrix have the minima. Titanium has systematic negative correlations with F, XMg, and (OH + F + Cl), whereas Al and octahedral vacancies are virtually constant.

These trends indicate that the Ti-vacancy, along with substitutions involving Al, cannot explain the observed short-scale variations. Conversely, the Ti-oxy exchange appears to be active, resulting from combination of two vectors: the more conventional hydroxylation Ti4+ + 2O2– = (Fe,Mg)2+ + 2OH– and the “fluorination” Ti4+ + 2O2– = (Fe,Mg)2+ + 2F–. The systematic retrograde redistribution involves not only Fe and Mg as commonly observed, but also Ti, F, and H, in a way such to eliminate the primary Ti-oxy component of biotite.

Keywords: Biotite, crystal-chemistry, granulite, pegmatite, retrograde diffusion, titanium

INTRODUCTION

This paper is a continuation of Charlie Guidotti’s research on metamorphic biotite and is a logical extension of that earlier work to higher grades of granulite metamorphism and partial melting of metapelites. The behavior of Ti in biotite during prograde metamorphism was first summarized by Guidotti (1984): with increasing metamorphic grade Ti is progressively incorporated in biotite, reaching values of ca. 0.3 atoms/22 O atoms (i.e., ca. 2.5 wt% TiO2) in samples from the “upper sillimanite” zone. Subsequently, Charlie attracted several researchers (including the writers) who focused their efforts on the quantitative aspects of biotite crystal chemistry. The most recent result is the development of the Ti-in-biotite geothermometer (Henry and Guidotti 2002; Henry et al. 2005) for graphitic metapelites at 4–6 kbar. In the early 1990s, Guidotti and co-workers (in particular Darby Dyar) pioneered the quantification of Fe3+ (Dyar 1990) and H in biotite and other minerals from metapelites (Dyar et al. 1991, 1993) showing that the H content of micas is far from stoichiometric, and that direct measurement of H is necessary to properly model mineral formulae. In the case of biotite, Dyar et al. (1991) showed that the Ti increase is mirrored by a continuous decrease of H, suggesting that deprotonation mechanisms may occur during prograde metamorphism.

Based on a series of amphibolite-facies samples from western Maine, the above work did not explore the behavior of biotite at very high temperature (HT) and anatexis, where the possible extent and effects of deprotonation should be maximized. In a previous study of partially melted metapelites, Cesare et al. (2003) showed that deprotonation, by way of the Ti-oxy exchange...