Experimental investigation of the Fe-Mgpartitioning between garnet and biotite with respect to the influence of Ti in biotite

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Introduction

The temperature dependent Fe-Mg-exchange between garnet and biotite provides an important geothermometer. It was calibrated empirically, theoretically and experimentally by several authors (e.g. Ferry & Spear, 1978; Thompson, 1976; Goldman & Albee, 1977; Perchuk et al., 1985). The application of these calibrations to natural assemblages however is restricted to certain compositions of the coexisting phases, since the effects of other substituting cations such as Ca and Mn in garnet or Ti, Al^{VI}, Fe³⁺ in biotite on the Fe-Mg-partitioning are not considered. Especially for rocks of granulite facies, the garnet-biotite temperature estimates show inconsistencies, as stated e.g. by Bohlen & Essene (1980). For a reliable application of the garnet-biotite geothermometer to natural assemblages, a precise quantification of the nonideal mixing properties of the involved phases is required.

The aim of this experimental study is to determine of the influence of Titanium substitution in biotite on the Fe-Mg-cation-exchange with garnet.

Experimental procedures

Starting materials are synthetic garnet ($alm_{80}py_{20}$, $alm_{70}py_{30}$) and natural biotite (IpFU A1 = 2.96, 2.23, 2.55; IpFU Ti = 0.30, 0.40, 0.64). The use of natural Ti-bearing biotites is necessary because the yields of synthesis of the required biotite are not sufficient (Abrecht & Hewitt, 1988).

Experiments were performed hydrothermally with 95:5 weight%-mixtures of garnet and biotite in the double capsule technique. By the choosen weight-ratio of the phases Fe-Mg cationexchange can be achieved below 800°C (Ferry & Spear, 1978). Run durations were about 350 to 600 h at temperatures between 600 to 800°C and water pressure of 0,2 GP. The water content varied between 5 and 10 weight% and the oxygenfugacity was controlled by the Co/CoO-buffer.

Portions of the run products were dispersed by a suspension-method on flat, artifical-resin surfaces and analysed by electronmicroprobe.

To ascertain that equilibrium has been attained, most garnet-biotite mixes were reground and rerun at the same conditions. Reversal exchange reactions were carried out for some runs, where corresponding natural biotite material (identical Ti-content, different Fe/Mg ratio) was available.

Results and discussion

The results of six series of isobaric exchange experiments at temperatures of 600 to 800°C indicate nonideal mixing behaviour for both minerals.

The Fe/Mg-ratios of garnet in the run products closely correspond to the starting compositions. For biotite the Fe/Mg-values shift in dependence of temperature. The total changes in biotite composition amount up to 34 mole% annite component. Compositional shifts of biotite in the rerun garnet-biotite mixtures are in the scale of only a few mole% annite, which indicates that equilibrium composition is approached. Ticontents of the biotites generally are slightly lower than in the starting material, but attain a constant value for each starting composition (IpFU Ti = 0.25, 0.34, 0.55) independent of garnet composition and temperature. Additional experiments with rutile or ilmenite as Ti excess phases result in corresponding Ti- contents of biotite.

Series of runs with fixed garnet compostion and various natural biotites (different Ti-contents) yield different $\ln K_D$ versus 1/T relations. Run products with Ti-rich biotite give lower Fe-Mg partitioning values than those with Ti-poor biotite. For each garnet composition three nearly parallel data sets with linear correlations of $\ln K_D$ versus 1/T are obtained. The systematics in the partitioning data provides evidence for nonideal

mixing in biotite. Ignoring possible effects arising from nonideal mixing behaviour of Al^{IV} , Fe and Mg, for a given K_D -value a difference of about 2 weight % TiO2 would correspond to a difference in temperature of approximately 100°C.

The partitioning experiments with Ti-bearing biotite show a much stronger temperature dependence of the Fe-Mg-exchange when compared with the experimental data of the Fe-Mg binary system studied by Ferry and Spear (1978) and also in comparison with the experimental data of Perchuk *et al.*, (1985). The amount of Ti in biotite does not affect the gradient of temperature dependence of lnK_D , which is deduced from the parallelism of all data sets.

The exchange experiments between biotite of constant Ti-content and garnet with different Fe/Mg-ratios result in two nearly parallel data sets. Run products with Mg-rich garnet give lower partition coefficients. Assuming ideal Fe-Mg mixing in biotite the lnK_D systematics at constant T are due to nonideal mixing properties of garnet. The observed effects of nonideality correspond to about 100°C for a difference of 10 mole% almandine component. Considering the garnet solution model of Berman (1990) lead not to convergence of the two obtained data sets and thus gives further evidence for nonideal mixing

behaviour in biotite.

A comparison of calculated temperature estimates obtained from the experimental data of this study for widley used calibrations reveals deviations from the experimental temperature up to + 380°C. This also holds true for the calibration of Indares & Martignole (1985), which takes into account Ti and Al interaction effects. Employing their model, the calculated temperature still deviates about ± 130 °C from the experimental temperature.

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