Short Communcations

UNUSUAL THERMAL BEHAVIOUR OF BIOTITES MT. PAPUK

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Results are presented from the DTA, TG and DTG examinations of three biotites from Mt. Papuk in Croatia, Yugoslavia. These biotites showed a continuous loss of weight throughout the entire temperature interval from 25 to 1200°.

Mineralogical researches on biotites from various Mt. Papuk rocks included thermoanalytical examinations of biotites from porphyroblastic gneiss, muscovite-biotite paragneiss (brook V. Radetina) and pegmatite (brook Brzaja).

According to Hunziker [1], Schwander *et al.* [2] and Smykatz-Kloss [3], biotites generally display three peaks. The first exothermic effect results from the oxidation of bivalent iron at approximately 400°, but can also appear at higher temperatures. The endotherm due to dehydroxylation occurs at approximately 600° and is sometimes overlapped by the oxidation exotherm. Smykatz-Kloss [3] reports yet another endothermic effect at approx. 860°, attributed to decomposition. The last endothermic effect is noticeable at a temperature over 1150°. Ivanova *et al.* [4] describe only two peaks, an exotherm in the temperature range 600–900°, due to bivalent iron oxidation, and an endotherm between 1100 and 1200°, caused by dehydroxylation and lattice destruction, as well as by phase transition into magnesioferrite. Mackenzie [5] mentions the "usually small event" at approx. 300–350°, the larger exotherm at approx. 700–800°, attributable to bivalent iron oxidation, and the endotherm of dehydroxylation at 1000–1200°, which moves to slightly lower temperatures in samples with higher contents of bivalent iron.

Pure biotite phases (diameter of powder flakes less than 4×10^{-3} cm) were simultaneously examined by differential thermal analysis (DTA), thermogravimetry (TG) and derivative thermogravimetry (DTG), using a Mettler thermoanalyser and a Pt-PtRh thermocouple. Thermoanalytical curves of the samples are given in Fig. 1. The DTA curves were corrected for the zero error. The biotite from porphyroblastic gneiss was also examined on a MOM derivatograph.

The examined biotites from Papuk exhibited quite an unexpected thermal behaviour. The curves of these biotites definitely indicate that the weight loss in the entire temperature range up to 1200° is an almost continuous process, except for the release of hygroscopic water. The total weight losses between 25 and 1200°

(after the oxygen content resulting from the Fe^{2+} oxidation was added, and the moisture content substracted) are in agreement with the chemical analysis data and with the content of OH^- ions in the structural formula of biotite.

The differential thermal curve is characterized by two endotherms: the first, at approximately 140°, corresponds to the release of hygroscopic water, and the second, at 1150°, is probably due to partial melting and lattice destruction.

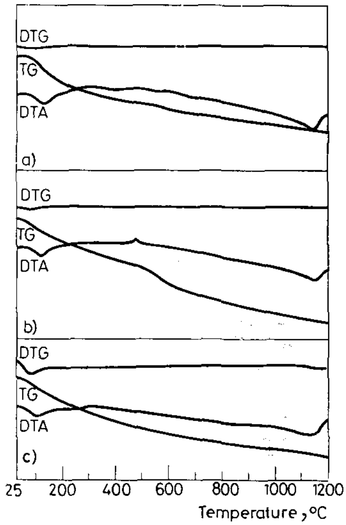

Fig. 1. Thermoanalytical curves of Mt. Papuk biotites: a) biotite from porphyroblastic gneiss, b) biotite from muscovite-biotite paragneiss, c) biotite from pegmatite

It should be noted that the derivative thermogravimetric curve is almost straight, except within the interval from 25 to 140°, indicating thus a continuous loss of weight in the temperature range from 140° onwards.

To check these findings, the biotite from porphyroblastic gneiss was first dried at 105° and then examined on the MOM derivatograph. In the temperature range from 25 to 1000° the DTA curve shows two exothermic effects of weak intensity (from 80 to 240°, and from 420 to 460°). The TG curve displays an almost continuous weight loss, the slope being more expressed between the two exothermic effects.

The results obtained indicate that the oxidation of iron (weight increase) and the dehydroxylation of the talc layer (weight loss) are almost continuous processes in these biotites until the phases have transformed into a molten mass.

Livova [6] observed a similar continuous weight loss in some biotites, but gave no explanation of the phenomenon.

X-ray diffraction analysis proved that the examined biotites from Mt. Papuk are well-crystallized, so the continuous dehydroxylation cannot be explained by different bonding energies of the OH^- ions. On the other hand, it is well known that in the process of biotite weathering, the oxidation of Fe^{2+} is accompanied by proton release from the OH^- ion [7]. It can be assumed that the same phenomenon occurs on heating. Such a process, however, would signify the energy release and the strengthening of the Fe–O bond, but this is not in agreement with the thermal behavior of the examined biotites, although the total energy balance necessarily includes the energy of OH^- dissociation.

A more complex research of the extraordinary thermal behaviour of these biotites is in progress.

References

1. J. C. Hunziker, Mineral. Petrogr. Mitt., 46 (1966) 473.
2. H. Schwander, J. Hunziker and W. Stern, Mineral Petrogr. Mitt., 48 (1968) 357.
3. W. Smykatz-Kloss, Differential Thermal Analysis, Springer-Verlag, Berlin (Heidelberg) New York, 1974.
4. V. P. Ivanova, B. K. Kasatov, T. N. Krasavina and E. L. Rozinova, Thermal analysis of minerals and rocks. Nedra, Leningrad, 1974.
5. Differential Thermal Analysis, ed. R. C. Mackenzie, vol. 1, Academic Press, London/New York, 1970.
6. I. A. Livova, Sites of USSR vermiculites. Nedra, Leningrad, 1974.
7. W. A. Deer, R. A. Howie and J. Zussman, Rock-forming minerals, 3. ed. Longmans, London, 1967.