

PARTITIONING OF TRACE ELEMENTS AMONG COEXISTING OPAQUE OXIDES IN APOLLO 17 BASALTS USING A PROTON PROBE MICROANALYZER. H. Blank⁺, R. Nöbling^x, K. Traxel^x, and A. El Goresy⁺, ⁺Max-Planck-Institut f. Kernphysik, Heidelberg, F.R. Germany; ^xPhysikalisches Institut der Universität Heidelberg, Heidelberg, F.R. Germany.

A series of opaque assemblages were recorded in the various types of Apollo 17 basalts (1,2). In the major basalt types, i.e. 1. plagioclase poikilitic ilmenite basalts, and 2. olivine porphyritic ilmenite basalts two distinct crystallization sequences were reported (1): spinel-olivine-armalcolite-pyroxene-ilmenite for 1 and spinel-olivine-armalcolite-ilmenite-pyroxene for 2, respectively. It was experimentally demonstrated that the inversion of the sequence armalcolite-pyroxene-ilmenite in 1 to armalcolite-ilmenite-pyroxene in 2 is due to differences in f_{O_2} during crystallization (3). Plagioclase poikilitic ilmenite basalts have crystallized accordingly under lower f_{O_2} values than olivine porphyritic basalts. Many of these primary assemblages were then modified at lower temperatures by subsolidus reactions, namely a) subsolidus reduction and b) subsolidus equilibration (2,4). Partitioning among the various phases of an assemblage is not confined to the major elements. Trace elements should likewise show such partitioning which is presumably temperature dependent. Some trace elements, e.g. Zr, were found to partition among ilmenite and ulvöspinel in favor of ilmenite in Fra Mauro rocks (5). Attempts to measure partitioning of Zr and other trace elements in opaque minerals in Apollo 17 rocks with the electron microprobe were unsuccessful since only rutile was found to contain detectable concentrations. The high level of the bremsstrahlung prevented analyses of Zr in different opaque minerals occurring in various assemblages. Exciting X-rays with a proton beam is favourable to electron beam excitation because of the low bremsstrahlung background of the protons (bremsstrahlung is proportional to $1/m^2$). Under these circumstances, X-ray spectra of trace elements in the sample could be quantitatively measured if an appropriate standard is used (6).

Using the Heidelberg proton microprobe analyzer (7) we have carried out detailed studies of opaque minerals in different assemblages in both plagioclase poikilitic ilmenite basalts and olivine porphyritic ilmenite basalts. The aim of the present investigations was to determine 1. the trace element content of the various minerals for a better understanding of the geochemical behaviour of these elements, and 2. the partitioning of certain trace elements among coexisting opaque oxides in the various assemblages in the two rock types. Major and minor element compositions of the minerals were measured at 15 keV with the electron microprobe. The same grains were then measured with the proton microprobe at 3 MeV proton energy and 120-160 pA beam current. The proton beam was focussed on the surface of the sample to sizes between $2 \times 4 \mu m^2$ and $6 \times 6 \mu m^2$. During a single run, changes in the beam size were not detected despite the long integration time (4000-6000 s). At the low beam currents used, the samples did not suffer from any degradation. A synthetic stoichiometric ilmenite with a Zr-concentration of 4370 ± 550 ppm was used as an internal standard. The Zr-ilmenite standard was also used for measurements of Nb, Sr and Y since the X-ray yield of these elements are quite similar to that of Zr. However, an Y-bearing glass was also applied for further calibration of the measured Y-concentrations. Due to similarity in total Z, matrix corrections are not necessary when the Zr-ilmenite standard was used. By only applying the Y-glass standard for Y results were 10% lower than those detected if the Zr-ilmenite is used. Due to the large penetration depth of the proton beam (30-40 μm) compared to the shallow penetration depth of the electron beam ($\sim 5 \mu m$), the excited volume in both experiments were not identical. This is a possible source of error

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since in some cases the area excited by the proton beam may lay below the mineral of interest. Calibration experiments using well defined multicomponent layered targets are in progress to accurately measure penetration depths of the proton beam at different proton energies and to calculate more efficiently the matrix corrections. An Al foil of 0.2 mm thickness was used as an absorber for the Si(Li) detector to reduce the FeK count rate to 30-60 Hz.

Results and Discussion. Coexisting armalcolite-ilmenite mineral pairs were measured in samples 70215,159; 72015,21; and 74242,19. The first two samples belong to the olivine porphyritic ilmenite basalt family. Sample 74242,19 consists of various lithic fragments >2 mm in which both rock types are present. The proton beam analyses revealed the presence of Sr, Y, Zr, and Nb in both armalcolite and ilmenite. Fig. 1 displays a spectrum obtained from an ilmenite grain in sample 70215,159 - indicating a high Zr, moderate Sr, Y, and low Nb concentrations. A step scan was performed on an armalcolite grain mantled by ilmenite to check for 1. zoning in the distribution of the trace elements, and 2. diffusion features at the ilmenite-armalcolite boundary. Fig. 2a is a photomicrograph of the composite grain studied showing the location of the analysed points in both minerals. Fig. 2b is an SEM photograph of the lower right corner of the composite grain with the carbon contamination spots of the electron beam (EB) and the proton beam (PB). The results are shown in Fig. 2c. Armalcolite shows clearly a higher Zr-concentration (up to 200 ppm) than ilmenite (~100 ppm). Two unique features can also be seen in this figure: 1. There is evidence of zoning in armalcolite with higher Zr-contents in the core than in the rim, and 2. ilmenite shows lower Zr-concentrations at the armalcolite boundary which we interpret as evidence for diffusion of Zr from ilmenite to armalcolite. The fact that despite this Zr-diffusion from ilmenite to armalcolite no enhancement of the Zr-concentrations were detected in armalcolite at the ilmenite boundary, may suggest that before the diffusion took place the Zr-zoning in armalcolite was steeper than detected. Analysis 6 (Fig. 2b,c) shows anomalously high Zr-concentration (~500 ppm). The analysis point is just at the armalcolite rim and is adjacent to a rutile grain in ilmenite. We believe that this high Zr-content is caused by contamination due to excitation of both armalcolite and rutile (2).

Comparative analyses of the Zr-partitioning between armalcolite and ilmenite in the two basalt types revealed a unique feature: In almost all analysed armalcolites rimmed with ilmenite in olivine porphyritic ilmenite basalts Zr partitions in favor of armalcolite (2 in Fig.3). In comparison, the Zr-content in ilmenite in plagioclase poikilitic basalt was found to be much higher than that of the adjacent armalcolite (1 in Fig. 3). This relationship may be considered representing the initial Zr-concentrations as defined by the crystallization sequence, i.e. Zr-diffusion if any from ilmenite to armalcolite in this basalt type was negligible. If this interpretation is correct, then the partitioning observed in olivine porphyritic basalts in favour of armalcolite was only initiated and accelerated by either 1. reaction between the basaltic liquid and armalcolite to form ilmenite and/or 2. subsolidus reduction and other subsolidus equilibration reactions (1,2,4). This result may have severe limitations to the application of the partitioning of Zr between coexisting phases as an absolute cooling rate indicator. It is not known if the ilmenite-ulvöspinel pair behaves similarly. Detailed investigations are in progress. The Zr-content in ulvöspinel was found to be much lower (average 80±25 ppm) than the concentrations in ilmenite and armalcolite.

Nb behaves similar to Zr in its distribution between armalcolite, ilmenite and ulvöspinel. However, Nb shows a higher partitioning in favour of armalcolite and ilmenite. The Zr/Nb ratio in armalcolite and ilmenite is close to 10, whereas in ulvöspinel it is about 16. Y and Sr do not show any particular pre-

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ference to any of the three minerals. The average Sr-content of the three minerals was found to be close to 70±22 ppm. The Y-content is about 50±15 ppm.

References. (1) El Goresy A. et al. (1974) Proc. Lunar Sci. Conf. 5th, p. 627. (2) El Goresy A. and P. Ramdohr (1975) Proc. Lunar Sci. Conf. 6th, p. 729. (3) Usselman (1975) Lunar Sci. VI, 164. (4) El Goresy A. and P. Ramdohr (1977) Proc. Lunar Sci. Conf. 8th, p. 1611. (5) El Goresy A., P. Ramdohr and L.A. Taylor (1972) Proc. Lunar Sci. Conf. 3rd, p. 333. (6) Bosch F. et al. (1978) Science 199, 765; Chen et al. Preprint MPI H - 1980 V13.

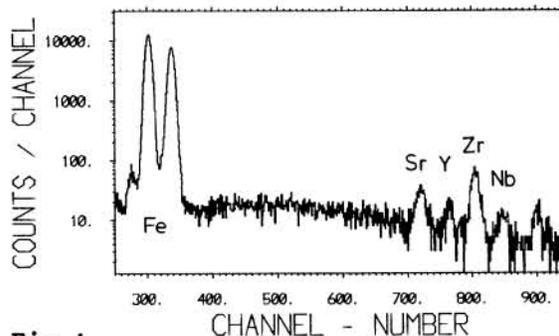


Fig.1

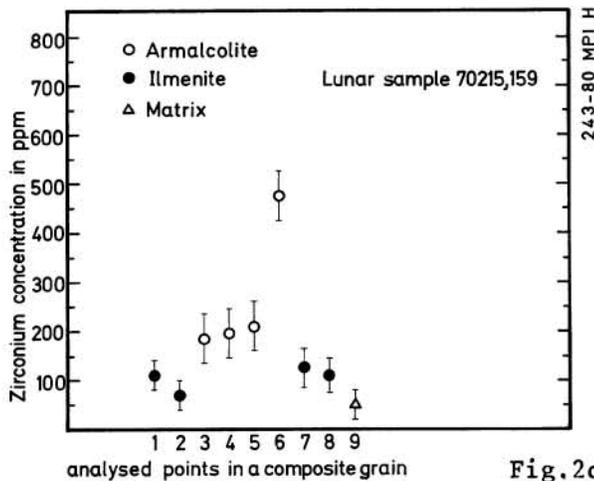
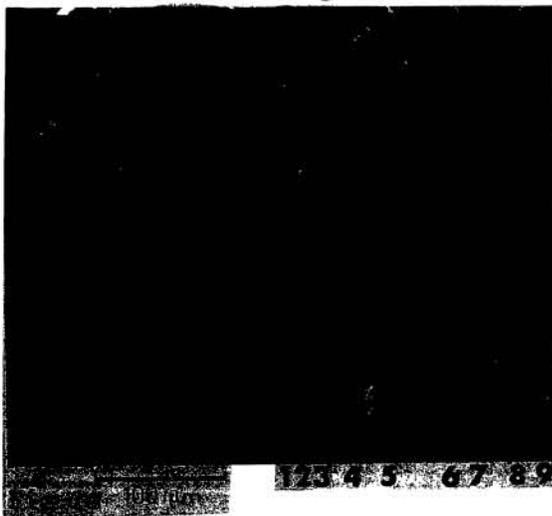


Fig.2c

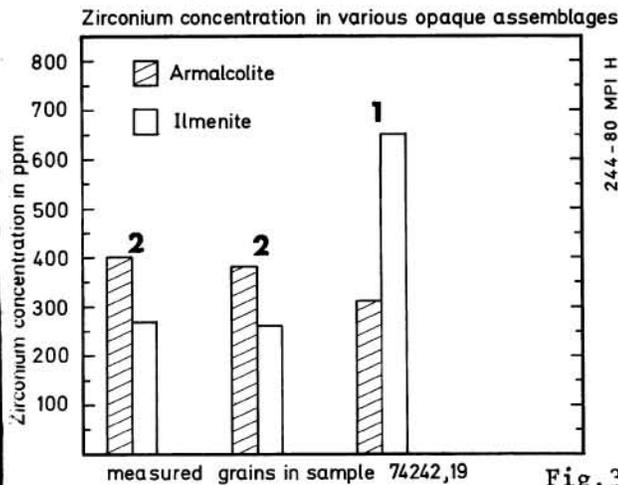
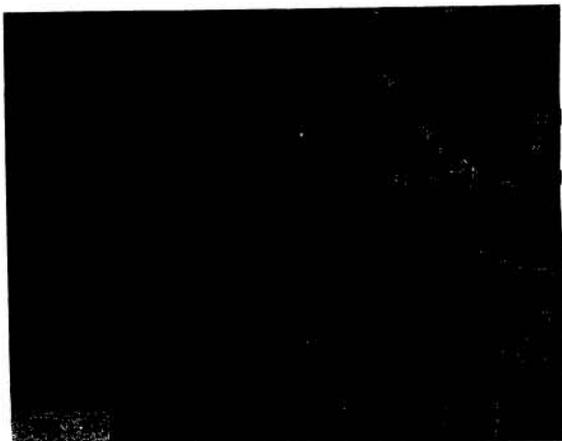


Fig.3