SOURCE OF ERRORS IN DEFOCUSSED BEAM ANALYSIS WITH THE ELECTRON PROBE, REVISITED.

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Introduction. "Broad beam" or "defocused beam" analyses (DBA) with the electron probe have been used extensively to study a chemistry of small lunar and meteorite samples [1-14]. The source and magnitude of errors in DBA data were discussed by Albee et al. [5], who showed that DBA method with usual homogeneous correction cannot be utilized for analysis of heterogeneous target. Reduction procedure recommended by Albee group takes into account the abundance of mineral phases as the essential factor in reducing of DBA data. In this paper we examine DBA method in theoretical and experimental views and show that reduction procedure [5] is erroneous. Other mode of correction is more appropriate.

Theory. According to [6] the concentration of oxide A0(CI) in the homogeneous target is:

\[ C_{I}^{w} = ( \rho_{u} \cdot K_{u} \cdot C_{I}^{u} \cdot (K_{I} \cdot \rho_{s} \cdot C_{I}^{s}) ) / (\rho_{s} \cdot K_{s} \cdot C_{I}^{s}) = \rho_{u} \cdot K_{u} \]

(1)

where \( \rho_{u} \) and \( \rho_{s} \) are correction factors for unknown and working standard, respectively, \( K_{u} \) and \( K_{s} \) refer to observed counts for the unknown and working standard, respectively, and \( C_{I}^{w} \) is the concentration of oxide A0 in standard. Analogously, it may be postulated that the concentration of oxide A0 in the heterogeneous target is:

\[ C_{I}^{h} = \rho_{u} \cdot K_{u} \cdot C_{I}^{u} \cdot (K_{I} \cdot \rho_{s} \cdot C_{I}^{s}) / (\rho_{s} \cdot K_{s} \cdot C_{I}^{s}) = \rho_{s} \cdot K_{s} \]

(2)

Albee et al. [5] suggested the expression for heterogeneous correction factor (\( \rho_{h} \)) in the following form:

\[ \rho_{h} = (C_{I}^{u} \cdot P_{I} \cdot C_{1}^{u} \cdot P_{1} \cdots C_{n}^{u} \cdot P_{n} + ... + C_{I}^{s} \cdot P_{I} \cdot C_{1}^{s} \cdot P_{1} \cdots C_{n}^{s} \cdot P_{n}) / (C_{I}^{u} \cdot P_{I} \cdot C_{1}^{u} \cdot P_{1} \cdots C_{n}^{u} \cdot P_{n}) \]

(3)

where \( C_{I}^{u} \) is the concentration of oxide A0 in phase n, \( P_{n} \) is the abundance of phase n expressed perhaps in weight proportion, and \( \rho_{h} \) is the homogeneous correction factor (see eq.(1)). On the other hand, it is very well known that:

\[ C_{I}^{h} \cdot P_{I} \cdot C_{1}^{h} \cdot P_{1} \cdots C_{n}^{h} \cdot P_{n} = C_{I}^{h} \cdot C_{I}^{h} \cdot C_{1}^{h} \cdot C_{1}^{h} \cdots C_{n}^{h} \cdot C_{n}^{h} \]

(4)

or taking into account the eq. (1):

\[ C_{I}^{h} \cdot K_{I} \cdot P_{I} \cdot K_{1} \cdot P_{1} \cdots K_{n} \cdot P_{n} = C_{I}^{h} \cdot K_{I} \cdot C_{I}^{h} \cdot C_{1}^{h} \cdot K_{1} \cdot C_{1}^{h} \cdots K_{n} \cdot C_{n}^{h} \]

(5)

if the count data (\( \rho_{h} \)) is:

\[ \rho_{h} = K_{I} \cdot P_{I} \cdot K_{1} \cdot P_{1} \cdots K_{n} \cdot P_{n} \]

(6)

then eq. (2) with \( \rho_{h} \) such as (3) equates to eq. (5) only in two cases. The first is monomineralic target (\( P_{n} = 0 \) when \( n = 1 \)). The second realizes when oxide A0 is concentrated in the one phase exclusively (\( C_{I}^{h} = 0 \), when \( n = 1 \)). In general case eq. (2) with \( \rho_{h} \) (3) and \( \rho_{h} \) (6) can not equate to eq. (5) or (4). Thus, the reduction procedure of DBA data on the basis of eq. (2) is not possible. Moreover eq. (6) is not obvious. Alternatively it may be assumed that \( \rho_{h} \) is connected with the volume proportions (\( V_{n} \)) of phases (more exactly with area proportions), but not with weight proportions, e.g.:

\[ \rho_{h} = K_{I} \cdot P_{I} \cdot K_{1} \cdot P_{1} \cdots K_{n} \cdot P_{n} \]

(7)

that is more difficult for correction of DBA data in form (2). For resolution of this alternative the experimental data about the relation between \( K_{I} \), \( V_{n} \) and \( P_{n} \) are necessary.

Experiments. We determined \( K_{I} \), \( V_{n} \) and \( P_{n} \) values for the tridymite-fayalite (\( Fe_{2}Al_{5} \)) association in Luna 24 basalt 1581 described by [7]. \( K_{I} \) and \( K_{h} \) data were obtained using a Hitachi Model XFA-60 electron microprobe with 38° take off angle operated at 15 kV, 0.04/4 A and 10-100μm diameter beam. Suitable \( V_{n} \) and \( V_{I} \) values were defined by area measuring in the ranges of the smf spots generated by electron beam. The values of \( P_{I} \) and \( P_{n} \) were recalculated from \( V_{I} \) data using the density of the phases. Results of our experimental work are compared on Fig. 1 with theoretical lines of the types (6) and (7) calculated from mineral chemistry data and it is obvious that only eq. (7) is satisfactory to the experimental data. This provides a way of calculating target chemical composition by: 1) resolution eq. (7) relative to \( V_{n} \) values using mineral chemistry data \( K_{n} \) or \( K_{n}^{w} \) data and 2\( V_{n}^{I} \); 2) transformation obtained \( V_{n} \) to \( P_{n} \) values; and 3) calculation of \( K_{n} \) according to eq. (4) or (5). The results of this calculation for 40μm diameter beam are presented in Table 1 (col.2). When compared with the results of the homogeneous and heterogeneous [5] corrections of the same DBA data (Table 1, col.3 and 4 respectively) the such reduction procedure leads to very good approximation of real composition (Table 1, col.1).

Discussion. Thus, we conclude 1) count data (\( K_{I} \)) for heterogeneous target are connected with the volume proportions of phases but not with weight proportions that must increase the element contents of \( V_{n} \) data (Table 1) and correspond to the character of empirical factors reported by [2]; 2) correction of DBA data is only possible on the basis of eq. (7) and eq. (5). Evidently, the same additional information is needed for the resolution of eq. (7), for example the composition of some phases or the \( V_{n} \) values. If the phase chemistry are completely known then DBA method is in fact mode of determination of the phase abundances and only on this basis the chemical target composition can be determined. Usually neither the phase chemistry nor \( V_{n} \) data are known. In this case the simplest compositions of CIPW normative minerals may be used, if of course the such approximation is acceptable. For example, reduction procedure of DBA data for the lunar type target, which consists of ilmenite, chromite, feldspar, olivine and pyroxene (\( Ca_{x}Mg_{y}Fe_{z}Si_{4}O_{10} \)) demands the solution of equation system including 1) equations (7) for all elements; 2) equations (1) for all minerals and all elements; 3) usual expressions...
for all β (63; 4) equations of stoichiometry for all phases assuming that Fe/Fe+Mg ratio is identical for olivine and pyroxene, and 5) FeO=100. This system may be resolved from DBA data relative to Vn values and chemical composition of feldspar and mafic minerals. Hence bulk composition may be also calculated from eq. (4) or (5) by changing Vn to Pn. The most difficult in this solution is determination of mafic mineral parameters. While ilmenite, chromite and feldspar parameters are calculated from K'M, K`M, and K'V, data very simply. The calculation of mafic minerals may be simplified by: 1) reduction of K`M data, which remain after subtraction K'M values of opaques and feldspar, using traditional homogeneous correction; and 2) normative recalculations of the obtained mafic composition for receiving the abundances and the compositions of olivine and pyroxene. This simplified method should not bring to large errors, because the densities of olivine and pyroxene are close. Results of such model calculations for VMA basalt (8) (Hitachi electron probe, 15KV) using the general and simplified methods are presented in Table 2 (col. 2 and 3 respectively). Both these versions are realistic relative to the true basalt composition (col. 1) excluding higher (than true) Ti and Cr contents. It means that the suggestion about the occurrence of Ti and Cr in only the opaques is erroneous. In order to correctly estimate Cr and Ti contents the additional data about their distribution in the rock are necessary, for example modal contents of the opaques. Homogeneous and heterogeneous (5) corrections, as it was suggested above, lead to increasing of feldspar elements and decreasing of mafic elements (col. 4 and 5 respectively).

Thus DBA method may be utilized for analysis of rock samples with reduction procedure on the basis of eq. (6) and eq. (7). If the necessary and correct data for resolution of these equations are absent then DBA method must bring to the mistakes. Possible petrological issues of these mistakes and other constraints in DBA analysis were considered by [53]. However, if the densities of phases in target differ a little, as for usual silicates, then errors of DBA even with homogeneous correction are not significant (Table 2) relative to usual accuracy geochemical conclusions and to the wish to know something about chemistry of small rock objects.