

Platy phlogopite from blast-furnace slags

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ABSTRACT. Phlogopite mica has crystallized from blast-furnace slags at atmospheric pressure. Its chemistry is characterized by an excess of Na and K over their normal stoichiometric content, which is attributed to a composite association between phlogopite and glass. The diffraction pattern indicates that the phlogopite has a preferred orientation around the *a*-axis. Scanning electron microscopy shows that this phlogopite consists of numerous small platelets, which probably have their *a*-axes aligned.

PHLOGOPITE mica, with unusual mineralogical features, has been found in some blast-furnace slags from the Port Talbot works of the British Steel Corporation. The chemistry of these slags belongs largely to the quaternary system CaO-MgO-Al₂O₃-SiO₂, but additional oxides lead to the crystallization of phases outside this system. Blast-furnace slags are cast into approximately hemispherical ladles 2 m in diameter and allowed to air-cool for two days. Samples were obtained from the coarse-grained interiors of the solid slags.

In thin section this mica forms as a pale blue to colourless pleochroic mineral which has extinction parallel to the trace of the (001) cleavage. It possesses second-order blue interference colours ($\delta = 0.017$), and is negative biaxial with a low 2V. The phlogopite crystallized as a groundmass mineral between melilite phenocrysts, forming as thin tabular crystals (up to 0.75 × 0.30 mm in size). The otherwise hollow vesicles within these slags often contain similar mica crystals.

Mineral chemistry

The mica chemistry (Table I) was determined with a CSI Microscan 9 electron microprobe; on-line computer corrections for ZAF effects were applied to all raw data. A natural phlogopite was analysed at the same time as these micas to check for analytical deviations. The composition of this natural phlogopite (Table I) remained approxi-

mately constant and is close to the stoichiometric formula.

The electron microprobe analyses indicate that there is an excess of Na, K, and Al, and a deficiency of Si relative to natural phlogopite. Less significantly, the CaO and MnO contents are also higher than in natural phlogopite.

The calculated formulae are close to

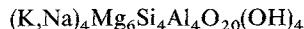


Table I Representative electron microprobe analyses of phlogopite from samples 1388, 1393, 1385, 1369 and 1886; the composition of a natural phlogopite (from a phlogopite megacryst in a De Beers kimberlite, IK9, supplied by Dr K.G. Cox) is given for comparison.

Analysis Number	1388G	1388V	1393G	1393V	1385G	1369G	1886G	Natural Phlogopite
SiO ₂	28.02	28.07	25.65	25.51	28.38	29.16	28.91	40.91
Al ₂ O ₃	20.97	20.74	22.33	22.93	21.44	20.25	20.35	11.86
TiO ₂	1.54	1.45	3.30	3.17	1.52	1.13	1.04	1.30
MgO	24.60	25.42	23.56	23.59	25.36	25.51	25.34	24.99
FeO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.01
MnO	0.12	0.19	0.55	0.55	0.11	0.37	0.09	0.01
CaO	0.12	0.10	0.28	0.38	0.09	0.10	0.08	0.00
Na ₂ O	3.13	2.83	6.08	7.46	3.02	1.95	1.89	0.16
K ₂ O	14.57	14.36	10.73	8.68	14.73	15.54	15.91	10.54
Total	93.07	93.16	92.48	92.27	94.65	94.01	93.61	93.78
NUMBER OF CATIONS FOR 22 OXYGENS (anhydrous state)								
Si	4.26	4.25	3.91	3.87	4.24	4.39	4.38	5.90
Al	3.76	3.70	4.01	4.10	3.78	3.60	3.63	2.02
Ti	0.18	0.17	0.38	0.36	0.17	0.13	0.12	0.15
Mg	5.57	5.74	5.35	5.33	5.65	5.73	5.72	5.39
Fe	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.48
Mn	0.01	0.02	0.07	0.07	0.01	0.05	0.01	0.00
Ca	0.02	0.02	0.05	0.06	0.01	0.02	0.01	0.00
Na	0.92	0.83	1.80	2.19	0.88	0.57	0.56	0.04
K	2.83	2.78	2.09	1.68	2.81	2.99	3.07	1.94
Σ	17.55	17.51	17.66	17.66	17.55	17.48	17.50	15.92

NOTE G = phlogopite from the groundmass

V = phlogopite from the vesicles (samples 1388 and 1393 only)

Water content: (i) There was insufficient material for the determination of the water content of the slag phlogopites.

(ii) The water content of the natural phlogopite has been determined as H₂O⁺ = 5.13 wt%
H₂O⁻ = 0.02 wt%

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and so deviate significantly from ideal stoichiometric phlogopite. There seem to be two possible explanations for this unusual composition:

1. That the crystals are a single phase with this composition, which has been derived from phlogopite by insertion of excess $(K,Na)^+$ and substitution of Al^{3+} for Si^{4+} . However, the formula is a most unlikely one for a mica whose structure does not have any sites to accommodate the excess (K,Na) . Such an unusual composition merits examination by diffraction methods to determine the structure and unit.

2. That the main crystalline phase has a composition close to phlogopite, $K_2Mg_6Si_6Al_2O_{20}(OH)_4$, and is submicroscopically intergrown with another phase richer in alkalis and Al, and poorer in Si. X-ray diffraction should then show a normal phlogopite mica as the main crystalline phase.

Single-crystal X-ray diffraction

A c -axis rotation photograph was taken of a mica crystal extracted from a vesicle of sample 1388. The recorded reflections do not form layer lines for the c -dimension, but define a series of rings forming sectors parallel to the camera axis. This is a texture pattern, which shows that the mica is composed of crystallites with a preferred orientation along an axis [UVO], most likely a or b . The axis along which the crystallites are aligned has been identified as a from the differences in ξ -value measured along the equator of the lines on the texture pattern.

The mica crystal was then orientated for the a -axis rotation photograph, although it is not known if this is the true a for the monoclinic cell. Each ring of the resulting texture pattern is made up by a number of arcs, and every arc is centred about a reflection. This extension of the reflections along powder arcs is caused by misalignment of the a -axes of the crystallites. The short lengths of these arcs suggest a misalignment of no more than 10° (Dr G. Cressey, pers. comm.). These powder arcs can be removed by keeping the mica crystal stationary: the spread of orientations about the aligned a -axes of the crystallites will enable an oscillation-type photograph to be obtained from the stationary crystal. Therefore, a series of these photographs was taken to obtain all possible reflections. To index these reflections a reciprocal lattice was constructed from the unit cell dimensions for the MgO end-member phlogopite (Deer, *et al.*, 1966), where $a = 5.314$, $b = 9.204$, $c = 10.314$, and $\beta = 99^\circ 54'$.

Determination of the unit cell parameters. The a dimension of the unit cell can be obtained directly from the oscillation-type photographs, whilst the b

dimension can be calculated from the $0k0$ reflections. The displacement of the origin on successive levels in the reciprocal lattice can be measured enabling calculation of an approximate value of β .

Since mica is pseudotrigonal the rotation axis may not be the true a for the monoclinic cell, but along one of the pseudo- a -axes, $[\bar{1}10]$ and $[\bar{1}\bar{1}0]$, at $\pm 120^\circ$ to the true a -axis of the monoclinic cell. The true a for the monoclinic cell cannot be established and so the cell dimensions may be those of one of the two monoclinic cells defined by the pseudo- a - and pseudo- b -axes. However, this distinction can be ignored because the determination of the cell parameters is only approximate.

The c dimension is different among one-, two- and three-layer polytypes, and so an independent determination of this value is required. A mica crystal from sample 1388 was used to obtain a diffraction pattern by the Gandolfi camera. The $00l$ reflections tend to be enhanced in micas, and it is most likely that c will be approximately either 10.3 Å or 20.6 Å. Using the a , b , and β values from the oscillation-type photographs in association with these two c values, an attempt can be made to index the Gandolfi diffraction pattern. Using $c \sim 10.3$ Å leaves many lines unindexed, whereas using $c \sim 20.6$ Å allows all lines to be indexed. This suggests that the mica has a $2M$ structure, with an approximate c -spacing of 20.6 Å.

Therefore, a new reciprocal lattice was drawn, and the reflections on the oscillation-type photographs re-indexed. The b and β values were re-determined. The value $c \sin \beta$ can be measured from the $00l$ reflections, and since β is known the c dimension of the unit cell can be calculated. Therefore, approximate cell dimensions of $a = 5.3(7)$, $b = 9.1(8)$, $c = 20.6(1)$ Å, and $\beta = 96^\circ (21')$ were calculated from the single crystal photographs. Although only approximate, these values give some understanding of the phlogopite structure.

Hazen *et al.* (1981) found a phlogopite mica with Na in the octahedral layer; this suggests that some of the sodium in the slag phlogopite could be present in the octahedral sites. However, the calculated unit cell dimensions correspond to an ordinary phlogopite. Therefore, this slag phlogopite must be submicroscopically intergrown with another phase. As no other crystalline phase can be detected on the X-ray photographs, this second phase is most probably a glass.

Electron microscopy

To provide further information about this mica doubly polished sections of sample 1388 were prepared for transmission electron microscopy (TEM). The ion-thinning process was complicated

by the small amounts of mica within these sections, and resulted in many failures. When examined by TEM the mica crystals were all opaque to the electron beam, and so prevented further work.

An alternative approach involved grinding some mica flakes (from the vesicles of sample 1388) to a very fine size with a pestle and mortar. The ground mica was then finely suspended in water; a few drops of the suspension were placed on a copper grid for examination by TEM. This method produced mica flakes which were transparent to the electron beam.

Analysis by TEM involves an error of $\pm 0.5\%$ for each element, and sodium cannot be measured. Because of the importance of sodium (from Table I), no attempt was made to analyse the mica by this method. As K_2O is also in excess of the stoichiometric formula, the potassium concentration can be used to detect high alkali areas which would represent the glass (i.e. the second phase). No such areas could be found by TEM, although the glass may only be present in small amounts.

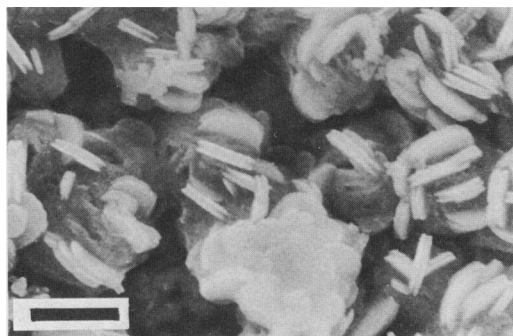


FIG. 1. SEM photograph showing mica platelets disorientated about the c -axis. Scale-bar represents $5\ \mu\text{m}$.

Investigation for glass. Mica crystals from the vesicles of sample 1388 (including the mica used for the single-crystal investigation) were studied by a scanning electron microscope (SEM). No preferred orientation could be found within any of the crystals. If the electron microprobe analyses are represented by phlogopite + glass, then it should be possible to etch the glass and so leave the mica crystallites. Some mica crystals were etched in glass cleaning solution (5% HF, 30% HNO_3 , 65% H_2O) for 3 hours, and then studied by the SEM. The resulting mica structure (fig. 1) appears to consist of numerous small platelets (up to $1\ \mu\text{m}$ in thickness) which are often disorientated about the c -axis. The individual platelets seem to be stacked on top of each other. It is probable that the preferred orienta-

tion on the diffraction pattern is produced by these platelets.

Preferred orientation in other micas

Rutstein (1979) described fine, acicular intergrowths of muscovite and chlorite in shear zones of chlorite-grade strata. Dr G. Cressey (pers. comm.) has found metamorphic muscovite (preferred orientation along the b -axis) with an acicular habit. In these two examples the preferred orientation of the mica appears to be produced by an acicular structure.

The intergrown mica of Rutstein has a preferred orientation along either the a -axis or the b -axis, and the a -axis is probably the dominant direction. 'This orientation is believed to be due to crystal growth into an opening shear zone. Orientated seed crystals in the phyllite matrix initiated growth mainly along the a -axis, and subsequent interference with neighbouring crystals is considered to have limited growth in the c and one other direction.'

Origin of the phlogopite

Petrographic relationships indicate that the phlogopite crystallized as a late-stage phase. Mica has also adhered to the sides of vesicles, which suggests a gaseous origin. However, the complex composition and the presence of such involatile components as TiO_2 , SiO_2 , and CaO would suggest that the mica in the vesicles must have crystallized from the residual liquid. Therefore, the mica in the vesicles probably crystallized at the contact between the residual liquid and gas bubbles.

Electron microprobe analysis showed that chlorine is absent, but that fluorine is probably present. Facilities were not available for water determinations from the small quantities of mica that could be extracted. However, the elements OH and F are required by the phlogopite formula. They may have come from the gas in the bubbles or have been dissolved in the residual liquid: it is not possible to say which.

The successful etching of the mica would seem to indicate that the high alkali content is associated with glass. This glass is probably formed in conjunction with final quenching of the liquid. The compositions and proportions of the glasses would be expected to vary, and so produce wide variations in the phlogopite-glass composite analyses: from inspection of Table I, however, this is not the case. As blast-furnace slags do not have similar residual liquid compositions (Wearing, 1981), this limited composite range suggests that phlogopite can only crystallize from residual liquids whose composition lies in a particular range. Since the phlogopite

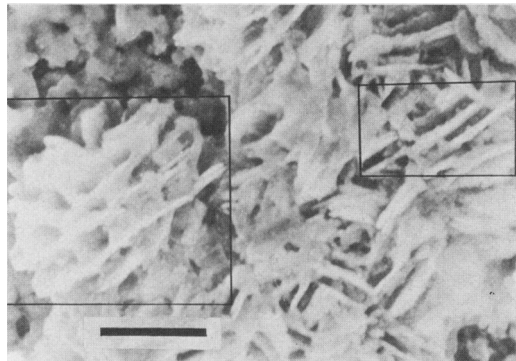


FIG. 2. SEM photograph showing a linear pattern (insets) which may be a result of the orientation of mica platelets along the *a*-axis. Scale-bar represents 5 μm .

compositions are unknown, the proportion of glass cannot be determined.

The apparent complex chemical characteristics of this mica probably reflects the composition of the residual liquids. The residual liquids of these blast-furnace slags are known to be rich in TiO_2 , K_2O , Na_2O , and MnO (Wearing, 1981). Residual liquid trends show a depletion in CaO and SiO_2 , and an enrichment in MgO and Al_2O_3 . Therefore, the composition of this mica reflects the composition of the residual liquid from which it crystallized.

Experimental evidence bearing on phlogopite stability is sparse. These slags indicate that phlogopite can form at atmospheric pressure and at crystallization temperatures of 1000°C or less, although more evidence is required to demonstrate that it is stable under those conditions.

Origin of the platelets. The large number of

platelets in fig. 1 suggests a high nucleation rate. They are disorientated about the *c*-axis, although the diffraction work indicates that the platelets have their *a*-axes aligned. In fig. 2 some platelets are arranged in a linear pattern, which may be a result of the orientation of mica platelets along their *a*-axes. Although different growth rates for different crystal directions may affect the morphology (i.e. produce the thin platelets), they cannot control the orientation.

As the mica is often in association with melilite phenocrysts, the crystal structure of the melilite may control the orientation of phlogopite nuclei on its surface. After these primary nuclei have grown, secondary nuclei might form on their surfaces in a controlled orientation. This would explain why the crystallites align, but not the direction of alignment.

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