

Special Services Division

Petrographical Department

## Mineralogical Report

Provisional analyses of minerals and glasses from A.E.R.E.

by

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Provisional analyses of minerals and glasses in two samples (JD 189 and 209) supplied by J Dalton, AERE, Harwell.

### 1. Introduction.

Glasses of various compositions are being examined for their capacities to immobilise fission products and resist corrosion. As part of this programme two samples of glass containing different assemblages of crystals have been qualitatively analysed. Their initial bulk compositions are given in Table 1, the waste comprising 21 elements the most abundant of which are Mg, Al and Fe.

Table 1. Glass compositions

| Wt%                           | JD 189 | JD 209 |
|-------------------------------|--------|--------|
| Waste                         | 25.26  | 25.70  |
| SiO <sub>2</sub>              | 41.51  | 50.88  |
| Li <sub>2</sub> O             | 3.69   | 3.99   |
| Na <sub>2</sub> O             | 7.68   | 8.30   |
| B <sub>2</sub> O <sub>3</sub> | 21.82  | 11.12  |
| Formation temp.               | 900°C  | 1000°C |

### 2. Analytical procedure.

Analyses of glass and crystalline phases in polished sections were carried out using a Cambridge Instruments Geoscan electron microprobe fitted with a Link Systems energy-dispersive analyser and computer. The computer enables on-line correction of absorption, fluorescence and atomic number effects for simultaneous multi-element analyses. The lightest element which can be analysed quantitatively on this equipment is Na, although F can be detected when present in abundance. Detection limits for each element vary with composition of the specimen but are typically 0.05 to 0.2% of the element. The accelerating voltage used was 15 kV, with a specimen current of  $5 \cdot 10^{-8}$  amps.

### 3. Results.

A. JD 189. The glass is homogeneous in major element composition, all analyses showing major Si, lesser Na, Mg, Al, Fe, Mo, Zr, and Nd, with varying minor to trace amounts of Cs, La, Ce, Pr, Zn and Ni. Representative analyses are shown in Table 2. These analyses are all of clear areas of glass intermediate to the crystals, and no determinations of concentration gradients in the vicinity of the crystals have as yet been made. The low totals of the analyses indicate that light elements not detectable by the analyser, are present in the glass. Thus B, Li and OH<sup>-</sup> or H<sub>2</sub>O may make up the remainder of the glass.

Some elements are impossible to detect in low concentrations in the presence of large concentrations of certain other elements because of peak overlap on the spectrum. These include low Rb, Sr and Y with high Si, and low P with high Zr. The computer has a fitting routine to match peak profiles in an unknown with standard profiles. This generates a "fit index" figure, which helps to indicate the presence of unsuspected elements in compound peaks. Thus if, Zr and P were both present in a specimen, but only Zr was input as an analysed element a high fit index would result. (A fit index of <2.0 is considered to indicate that all elements present in quantifiable concentrations have been analysed). The "fit index" of each of the glass analyses show that no significant quantities of Rb, Sr, Y or P are present. There is also a peak search routine which indicates peaks outside the fitting region of the selected element set.

Table 2. Analyses of glass in samples JD 189 and JD 209.

|                                | JD 189 |       |       | JD 209 |       |
|--------------------------------|--------|-------|-------|--------|-------|
| Wt%                            | 1      | 2     | 3     | 1      | 2     |
| Na <sub>2</sub> O              | 7.52   | 8.10  | 7.93  | 8.62   | 8.60  |
| MgO                            | 3.06   | 3.34  | 3.16  | 4.07   | 4.31  |
| Al <sub>2</sub> O <sub>3</sub> | 5.95   | 5.52  | 6.29  | 5.37   | 5.30  |
| SiO <sub>2</sub>               | 47.51  | 48.98 | 50.15 | 54.13  | 54.14 |
| FeO                            | 2.80   | 2.60  | 2.73  | 2.15   | 2.31  |
| NiO                            | n.d.   | n.d.  | tr    | tr     | tr    |
| ZnO                            | 0.60   | tr    | 0.89  | 0.85   | 0.57  |
| ZrO <sub>2</sub>               | 1.80   | 1.89  | 2.02  | 1.65   | 1.66  |
| MoO <sub>2</sub>               | 2.19   | 2.11  | 2.25  | 2.10   | 1.77  |
| Ca <sub>2</sub> O              | 0.52   | 0.59  | 0.42  | 0.48   | 0.63  |
| BaO                            |        |       |       | tr     |       |
| La <sub>2</sub> O <sub>3</sub> | tr     | n.d.  | tr    | 0.58   | tr    |
| CeO <sub>2</sub>               | tr     | n.d.  | n.d.  | tr     |       |
| Pr <sub>2</sub> O <sub>3</sub> | tr     | tr    | tr    |        |       |
| Nd <sub>2</sub> O <sub>3</sub> | 1.25   | 1.28  | 1.32  | 1.75   | 1.82  |

n.d. - not detected      tr - trace.

Although the crystalline phases present have widely varying forms and compositions three main groups are distinguishable. Most of the crystals are less than the thickness of the section (30  $\mu$ m) and this hinders optical and analytical work.

Type 1. The largest crystals are equant colourless anisotropic grains up to 70  $\mu$ m diameter mostly discrete but some occurring in clusters with other phases. Some also have inclusions of other phases, commonly opaque grains. They have high concentrations of rare-earth elements, with Nd > La > Pr > Ce. Analyses are shown in Table 3. Pr is given as Pr<sub>2</sub>O<sub>3</sub> as the correction programme will only accept one valency state for each element in any one analysis; the standard used for calibration is Pr<sub>6</sub>O<sub>11</sub> and the totals given should only be taken as approximate concentrations. Mo is given as MoO<sub>2</sub>, as data for Mo<sup>6+</sup> was not in store at the time of the analyses. Low totals may be partly due to the presence of undetectable light elements.

Type 2. Radiating clusters of colourless prismatic and smaller, brown acicular crystals are present, often centred on a core of opaque granules. Analysis of these was difficult because of their very small size, and further work is necessary to distinguish the phases. Analyses in the region of the clusters are characterised by high Mg and low totals (Table 4). This suggests that at least one of the phases consists of Mg combined with a light element, possibly B.

Table 3 Analyses of Type 1 crystals in JD 189.

| Wt%                            | 1     | 2     | 3     | 4     | 5     |
|--------------------------------|-------|-------|-------|-------|-------|
| Na <sub>2</sub> O              | tr    |       |       |       | tr    |
| MgO                            | 0.32  |       | 3.74  | 0.67  | 2.31  |
| Al <sub>2</sub> O <sub>3</sub> | 0.32  | 0.38  | tr    | tr    | tr    |
| SiO <sub>2</sub>               | 21.86 | 22.03 | 20.20 | 21.83 | 19.88 |
| Cr <sub>2</sub> O <sub>3</sub> | tr    |       |       |       |       |
| FeO                            | tr    |       |       |       | 0.38  |
| ZrO <sub>2</sub>               | n.d.  | tr    | tr    |       |       |
| La <sub>2</sub> O <sub>3</sub> | 14.04 | 14.71 | 14.79 | 15.42 | 13.22 |
| CeO <sub>2</sub>               | n.d.  | 1.49  | 2.12  | 2.10  | 8.34  |
| Pr <sub>2</sub> O <sub>3</sub> | 11.49 | 11.29 | 10.82 | 10.04 | 9.86  |
| Nd <sub>2</sub> O <sub>3</sub> | 43.02 | 41.74 | 38.22 | 39.22 | 36.54 |

n.d. - not detected tr - trace.

Table 4 Analyses of Type 2 and Type 3 crystals in JD 189.

| Wt%                            | Type 2 |       | Type 3 |       |       |
|--------------------------------|--------|-------|--------|-------|-------|
|                                | 1      | 2     | 1      | 2     | 3     |
| Na <sub>2</sub> O              | 3.16   | 0.54  | 0.53   | 0.41  | 3.92  |
| MgO                            | 30.25  | 46.47 | 0.39   | 0.67  | 1.42  |
| Al <sub>2</sub> O <sub>3</sub> | 2.82   | 0.77  | 0.28   | tr    | 2.35  |
| SiO <sub>2</sub>               | 21.82  | 5.84  | 1.53   | 3.03  | 18.22 |
| Cr <sub>2</sub> O <sub>3</sub> | 0.27   | 0.24  | tr     | n.d.  | 0.94  |
| FeO                            | 1.34   | 0.57  | tr     | tr    | 1.34  |
| NiO                            | 1.67   | 2.52  |        |       |       |
| ZnO                            | 0.31   | 0.67  | 0.47   | 0.51  | tr    |
| ZrO <sub>2</sub>               | 0.60   | tr    | tr     | tr    | 0.48  |
| MoO <sub>2</sub>               | 0.87   | tr    | tr     | n.d.  | 0.87  |
| RuO <sub>2</sub>               |        | 0.39  | 96.95  | 0.75  | 63.46 |
| PdO                            |        | tr    | tr     | 98.35 | n.d.  |
| Nd <sub>2</sub> O <sub>3</sub> | 0.60   | tr    | 1.56   | 3.76  | 0.72  |

Type 3. Opaques range in size from less than 1  $\mu\text{m}$  up to 200  $\mu\text{m}$  in granular aggregates. These contain Ru and Pd as major constituents, usually in distinct segregations where both are present in the same opaque mass. Analyses are shown in Table 4. Results are inconclusive at present, but analytical totals, combined with reflected light properties suggest that Pd is usually present as the metal, whereas Ru may be in metal or oxide state.

B. JD 209. The glass is homogeneous in major element composition (Table 2), the most significant difference from JD 189 being the higher concentration of  $\text{SiO}_2$  and higher totals, as would be expected from the bulk composition.

Three distinct groups of crystalline phases are present.

Type 1. Colourless prismatic crystals of varying composition, but all having major Si and Mg. The form and composition of these suggests a possible similarity to Mg-orthopyroxenes. The variations in the minor element composition are partly due to intergrowths, inclusions and adhering crystals of other phases. (see Table 5).

Type 2. These are small equant crystals with strong relief, characterised by high Ce concentrations. The analyses also show Si, but it is uncertain at present because of the small size of the crystals whether this is in the Ce-rich phase, or the surrounding glass. These crystals also contain several elements in concentrations of the order of 1 wt% oxides. (see Table 6).

Type 3. Opaques (Table 7) are composed mainly of Ru and Pd, with other elements probably present in fine intergrowths. Analyses in larger areas of grey-blue reflecting opaques show that Pd is present as the metal and Ru occurs mainly in brownish non-metallic opaques, which give totals close to theoretical  $\text{RuO}_2$  composition.

Table 5 Type 1 orthopyroxene-like crystals in JD 209.

| Wt%                     |       |       |       |       |       |       |
|-------------------------|-------|-------|-------|-------|-------|-------|
| $\text{Na}_2\text{O}$   | 1.04  | 3.48  | 1.48  | 3.16  | 0.63  | tr    |
| $\text{MgO}$            | 22.77 | 17.18 | 22.51 | 18.30 | 25.61 | 26.87 |
| $\text{Al}_2\text{O}_3$ | 0.84  | 2.28  | 0.89  | 2.17  | 0.50  | 0.38  |
| $\text{SiO}_2$          | 57.29 | 56.57 | 57.30 | 56.49 | 57.32 | 57.56 |
| $\text{Cr}_2\text{O}_3$ | 2.87  | 1.89  | 2.16  | 2.27  | 2.65  | 2.50  |
| $\text{FeO}$            | 4.85  | 4.33  | 5.06  | 3.28  | 4.24  | 4.56  |
| $\text{NiO}$            | 2.14  | 1.56  | 2.18  | 2.39  | 3.21  | 2.58  |
| $\text{ZnO}$            | tr    | 0.44  | 0.41  | tr    | 0.50  | 0.72  |
| $\text{ZrO}_2$          | 0.62  | 1.06  | 1.04  | 0.88  | 0.89  | 0.67  |
| $\text{MoO}_2$          | tr    | 0.74  | 0.28  | 0.87  | tr    | tr    |
| $\text{RuO}_2$          |       |       | tr    | tr    | 0.31  | tr    |
| $\text{PdO}$            |       |       | 0.39  | n.d.  | n.d.  | n.d.  |

n.d. - not detected tr - trace.

Table 6 Type 2 Ce-rich crystals in JD 209.

| Wt%                            |       |       |       |
|--------------------------------|-------|-------|-------|
| Na <sub>2</sub> O              | 2.28  | 6.01  | 3.93  |
| MgO                            | 1.62  | 2.54  | 1.81  |
| Al <sub>2</sub> O <sub>3</sub> | 1.43  | 3.45  | 2.25  |
| SiO <sub>2</sub>               | 13.83 | 32.79 | 21.19 |
| FeO                            | 0.59  | 1.39  | 0.81  |
| NiO                            |       | tr    | tr    |
| ZrO <sub>2</sub>               | 1.82  | 1.56  | 1.80  |
| MoO <sub>2</sub>               | 0.38  | 1.35  | 0.65  |
| RuO <sub>2</sub>               |       | 2.84  |       |
| CeO <sub>2</sub>               | 77.22 | 45.95 | 67.10 |
| Pr <sub>2</sub> O <sub>3</sub> |       | 1.10  | 1.00  |
| Nd <sub>2</sub> O <sub>3</sub> |       | 1.75  | 2.61  |

Table 7. Type 3 opaque grains in JD 209.

| Wt%                            |        |        |        |       |       |       |
|--------------------------------|--------|--------|--------|-------|-------|-------|
| Na <sub>2</sub> O              | 0.43   | 0.68   | 0.57   | 1.84  | 3.90  | 5.89  |
| MgO                            | 0.73   | tr     | 0.24   | 0.71  | 1.50  | 2.65  |
| Al <sub>2</sub> O <sub>3</sub> | 0.32   | 0.47   | tr     | 0.70  | 2.03  | 3.22  |
| SiO <sub>2</sub>               | 2.30   | 3.01   | 1.22   | 7.00  | 20.88 | 31.26 |
| Cr <sub>2</sub> O <sub>3</sub> | tr     | 0.0    | 0.0    | 0.91  | 0.55  | 0.0   |
| FeO                            |        |        |        | 0.37  |       | 1.39  |
| NiO                            |        |        |        | tr    |       |       |
| ZnO                            |        |        |        | tr    |       |       |
| ZrO <sub>2</sub>               |        |        |        |       | 0.50  | 1.17  |
| RuO <sub>2</sub>               | 0.00   | 0.00   | 100.16 | 89.21 | 62.64 | 31.50 |
| PdO                            | 111.34 | 108.64 | 0.0    | 0.0   | 2.71  | n.d.  |
| Pd metal                       | 96.79  | 94.44  |        |       | 2.36  |       |
| Cs <sub>2</sub> O              | tr     |        |        |       | 0.39  |       |
| CeO <sub>2</sub>               |        |        |        |       |       | 16.94 |
| Nd <sub>2</sub> O <sub>3</sub> | 0.62   |        |        |       | 0.72  |       |

n.d. - not detected tr - trace.

#### 4. Conclusion.

These results represent a preliminary investigation into the nature of the products obtained with different bulk compositions. After optical and X-ray work further refinement of the chemical analyses will take place until the major phases are adequately defined and the destination of the most critical elements is established.