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New Cu-bearing Glass Standards for Electron Microprobe Analysis

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Abstract

Two Cu-bearing glass standards, NGCU-1 and NGCU-2, for electron microprobe analysis have been synthesized. The NGCU-1 glass contains 6.28-wt. % CuO in a base of Mg-Ca-Al silicate, and the NGCU-2 glass contains 1.74% CuO, 2.23% Ni_2O_3, 2.14% Co_3O_4, 1.06% SrO and 2.70% BaO. The glasses are homogeneous and do not show a significant compositional change described in terms of "Lineweaver mechanismŧ during electron beam bombardment. The glasses are useful as standards for electron microprobe analysis.

Introduction

Electron microprobe analyses of manganese micronodules, usually less than 1 mm in size, have been recently carried out by many researchers (e.g. Ohashi, 1985; Sugisaki et al., 1987; Sugitani, 1987 and Sawada, 1988). The manganese micronodules normally contain NiO, CoO, CuO and BaO as much as 2-4wt. %. The reliability in analyses of such minor elements by microprobe is dependent largely upon standard materials. The choice of pure metal, oxide and sulfide as a standard causes an extremely high count rate during the measurement of the standard intensity. This brings about some difficulties in the correction of counting-loss, because the dead time of the counting system may be extended or non-extended as pointed out by Reed (1975). Synthetic standards containing Cu and others in small amounts are urgent for the microprobe analysis of manganese micronodules. This paper describes two newly synthesized glasses for microprobe standards of Cu, Co, Ni, Sr and Ba.

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Synthesis

Two Cu-bearing glasses, NGCU-1 and NGCU-2, were synthesized. The source materials are reagent powder of SiO_2, Al_2O_3, MgO, CuO, Ni_2O_3, Co_3O_4, $CaCO_3$, $BaCO_3$ and $SrCO_3$. These materials are treated along the following lines and kept in a desiccator prior to mixing;

1) SiO_2, Al_2O_3 and MgO are dried in air at 950°C for 6 hours.
2) CuO, Ni_2O_3 and Co_3O_4 are dried in air at 200°C for 12 hours.
3) $CaCO_3$, $BaCO_3$ and $SrCO_3$ are transformed into oxides through heating in air at 950-1000°C for 6 hours and ground with an agate mortar.

The starting mixture for the NGCU-1 glass is prepared by weighting SiO_2, Al_2O_3, MgO, CaO and CuO on precision balance and mixing in an agate mortar, and that for the NGCU-2 glass by mixing of SiO_2, Al_2O_3, MgO, CaO, CuO, Ni_2O_3, Co_3O_4, SrO and BaO. Each of the starting mixture is placed in a Pt-crucible, and dried with a vertical quench electric furnace at 900°C for 2 hours to allow a complete degassing. The temperature is brought to 1500°C and kept at this maximum temperature for an hour. The furnace is turned off, and the crucible is cooled to about 1350°C before removing. Quenching is done by dipping the crucible into distilled water. We prepared the final glasses through multiple (three times) grinding and melting at 1500℃ in air.

Wet chemical analysis

The composition of the NGCU-1 glass was determined with a wet chemical method which includes gravimetry for SiO_2 and R_2O_3, and atomic absorption spectrometry for Al, Fe, Mg, Cu, Ca, Na and K. The analytical result is listed in column B of Table 1. Alkalis are not detected but a substantial amount of Fe (the high oxygen pressure in the furnace is thought to have resulted in ferric iron: 0. 17wt. % as Fe_2O_3) is detected from the NGCU-1 glass. Since no iron was added to the starting mixture (see column A of Table 1), Fe_2O_3 is interpreted to come from impurities in the source materials. The difference in weight percent CuO between the starting mixture (column A) and the final glass (column B) supports this interpretation. Another interpretation is that iron was introduced through contamination from the crucible and/or the furnace. The microprobe check shows that the Pt-crucible used for the melting had, indeed, been alloyed with iron.

The final glass is a little higher in the SiO_2 and $A1_2O_3$ contents, and lower in the MgO, CuO and CaO contents than the Starting mixture. The discrepancies, at least in part, may be ascribed to imperfect decarbonation of $CaCO_3$, presence of impurity in CuO, and/or hydration of MgO and CaO during grinding and mixing. We take the weight percent components determined through the wet chemical method as the true composition of the NGCU-1 glass.

Table 1. Compositions (weight per cent) of synthesized glasses (NGCU-1 and NGCU-2) for microprobe standards

	NGCU-1				NGCU-2	
	A	B	C		D	
SiO_2	52.59	52.69	52.7	(0.2)	46.8	(0.2)
Al_2O_3	13.17	13.22	13.2	(0.1)	22.5	(0.1)
Fe_2O_3	-	0.17	0.15	(0.02)	0.82	(0.04)
MgO	8.83	8.77	8.70	(0.1)	4.41	(0.03)
Ni_2O_3	-	-	-		2.23	(0.03)
Co_3O_4	-	-	-		2.14	(0.02)
CuO	6.47	6.31	6.28	(0.07)	1.74	(0.02)
CaO	18.94	18.73	18.8	(0.1)	15.7	(0.1)
SrO	-	-	-		1.06	(0.03)
BaO	-	-	-		2.70	(0.03)
Total	100.0	99.72	99.83		100.10	

A : expected composition of NGCU-1
B : wet chemical analysis of NGCU-1
C : average and standard deviation of 170 microprobe analyses on 17 chips of NGCU-1
D : average and standard deviation of 150 microprobe analyses on 30 chips of NGCU-2

Stability of glasses under electron bombardment

Silicate glasses are known to show changes in X-ray intensities with time of electron beam bombardment during microprobe analyses (e.g. Varshneya et al., 1966; Borom and Hanneman, 1967). A question arises: Are the present glasses sufficiently stable under electron beam bombardment to permit quantitative microprobe analyses? To know how the X-ray intensities vary with time, we monitor X-ray intensities for a long duration by irradiating a probed beam on a given spot of the glasses. Experimental conditions are 3mm diameter beam of 0.1μA current, 3μm diameter beam of 0.05μA current and 20μm diameter of 0.1μA current. Accelerating voltage is 15kV. X-ray intensities are recorded in every 40 second intervals during the irradiation, and normalized to zero time as;

$$I_t \ / \ I_{t=0} = \frac{\text{Average count rate between } (t - 40) \text{ and } t}{\text{Count rate at } t = 0}$$

where t is time in second. The count rate at t=0 is indeterminable; we measure the count rate through moving the sample at a constant rate, and take this as the count rate at t=0. The measurement is repeated more than ten times, and the arithmetic average of the

$I_t / I_{t=0}$ values is taken. A typical set of results is shown in Fig. 1, and the time-dependent changes of CuKα intensities under different current densities are compared in Fig. 2.

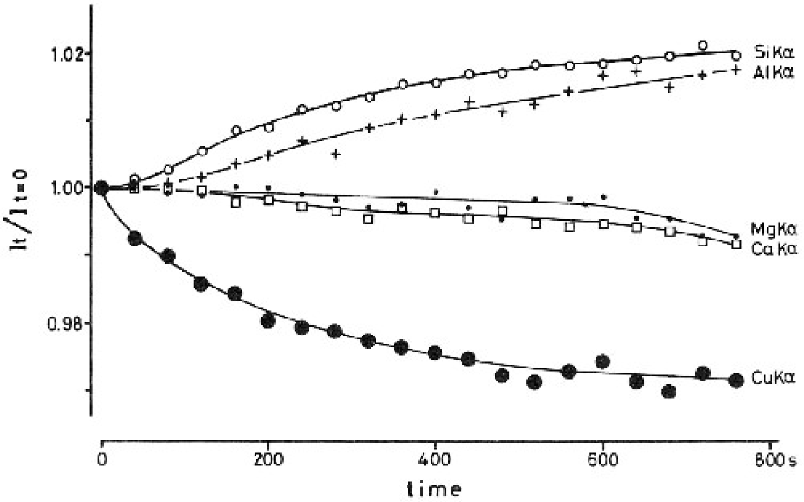

Fig. 1. Time-dependent changes of X-ray intensities from the NGCU-1 glass subjected to electron beam bombardment. The average count rate between (t-40) and t is taken as that at t, and normalized to zero time (see text).

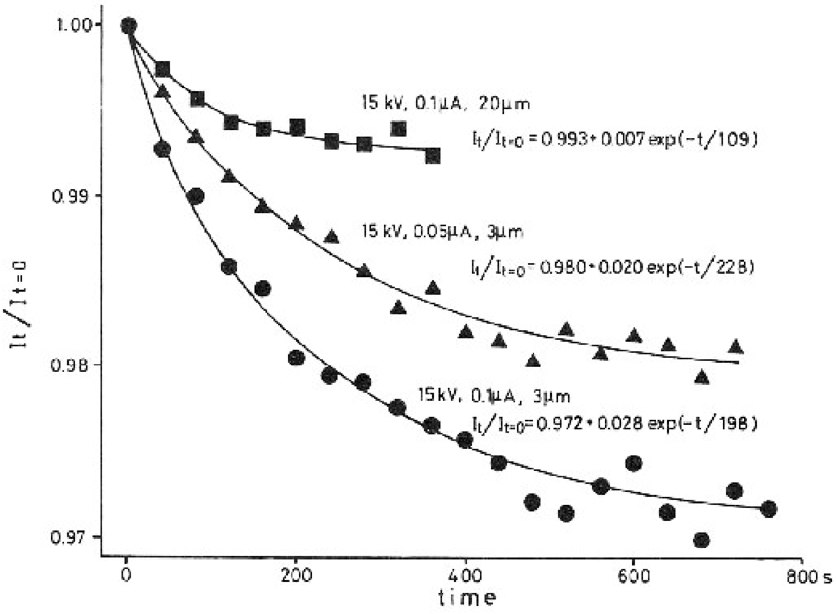

Fig. 2. Time-dependent changes of CuKα intensities from the NGCU-1 glass under different current densities of the electron beam. The X-ray intensities are normalized with those at zero time. The observed decrease in the CuKα intensity is fitted with an equation of the formula $I_t / I_{t=0} = A + B \exp(-t / K)$.

Figure 1 shows that the normalized intensity for CuKα decreases exponentially, increases for SiKα and AlKα, and is kept nearly constant for MgKα and CaKα. The intensity changes appear to be consistent with the Lineweaver mechanism (Lineweaver, 1963) that explains the effect of high electron flux on the evolution of oxygen from silicate glasses. Lineweaver suggested that incident electrons from the microbeam stop at some finite depth in glasses and form a zone of net negative charge underneath the surface. The field, established between the charged zone and the carbon conductive film, causes positively charged network-modifying cautions (e.g. Cu) to migrate toward the charged region. This process is accompanied by migration and evolution of nonbridging oxygens. The blistering effect of the carbon conductive film on the NGCU-l glass under the probed beam supports this interpretation. Migration of an ion from probed region to the charged zone causes a decrease in the fraction of that ion and an increase in the fraction of all other ions. Copper should be the most mobile cation in the NGCU-l glass; migration of Cu ions away from the probed region toward the charged region is probably a major cause of the observed decrease in the CuKα intensity. Network-forming silicon and aluminum should be the least mobile cation; their fractional concentrations in the probed region increase as the result of Cu migration and oxygen evolution. The compensation of the Mg- and Cu-migration effect with that of other ions should result in the approximate constancy of the MgKα and CaKα counts.

The NGCU-l glass yields more than 0.97 of the zero time CuKa intensity even after 600 second irradiation of a high density electron beam. The ca. 3% difference in X-ray counts between at t=0 and t=600 may be indistinguishable from the uncertainty owing to counting statistics on routine measurements. The NGCU-1 glass is practically acceptable for the microprobe standard. The time-dependent change of CuKα X-ray intensities of NGCU-2 glass is nearly the same as that of the NGCU-l glass. Figure 2 suggests that the inevitable intensity changes are minimized by keeping the electron density as low as possible while retaining sufficient X-ray intensity for the analysis, and by defocusing the electron beam to about a diameter of 20μm.

Homogeneity

The final glasses do not show any crystalline phase under the microscope. The homogeneity was examined by means of microprobe analyses. The operating conditions of electron microprobe are 15kV accelerating voltage, 3mm beam diameter and 0.015-0.03μA beam current. The X-ray intensity is integrated for 20 to 100 seconds. The measurement is repeated three times, and the arithmetic average is taken. The background is estimated from the offset readings on both side of each line-peak position. Analytical uncertainties are statistically estimated to be about 0.2wt. % for SiO_2, 0.1wt. % for Al_2O_3 and CaO, and 0.06-0. 03 wt.% for other components.

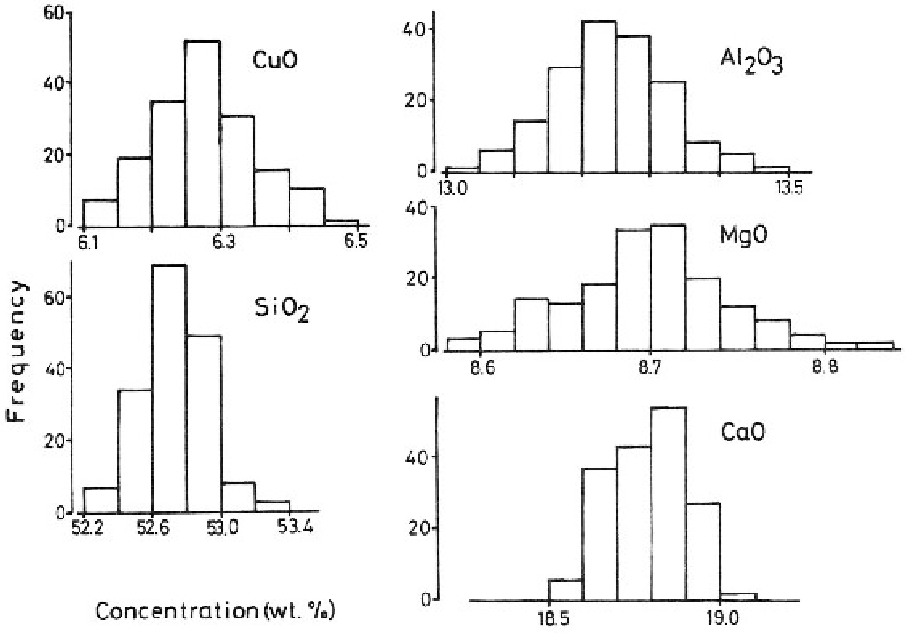

Fig. 3. Frcquency distribution diagrams of the CuO, SiO_2, Al_2O_3, MgO and CaO contents of 170 spot analyses on 17 different chips of the NCTCU-1 glass.

A total of 170 spot analyses were made on 17 chips of the NGCU-1 glass. The results are presented as frequency distribution diagrams (Fig. 3), and the average and standard deviation are listed in column C of Table 1. The frequency distribution of individual components shows a high kurtosis. The CuO contents range from 6.12 to 6.49 wt.%; the average is 6.27 wt.%. The analytical result coincides well with the wet chemical analysis (6.31 wt.%, column B in Table 1), and the standard deviation for CuO, 0.07, is approximately equal to the statistically estimated uncertainty (0.06 wt.%). The average compositions of SiO_2, Al_2O_3, Fe_2O_3, MgO and CaO also coincide with those determined with the wet chemical analysis, and the standard deviations for these components are nearly the same as the statistically estimated uncertainties. The NGCU-1 glass can be regarded as homogeneous one.

A total of 150 spot analyses were made on 30 chips of the NGCU-2 glass. The results are presented as frequency distribution diagrams (Fig. 4), and the average and standard deviation are listed in column D of Table 1. The oxidation states of Fe, Ni and Co are not determined, and hence they are conveniently expressed as Fe_2O_3, Ni_2O_3 and Co_3O_4, respectively. As shown in Figure 4, the 150 measurements on different chips do not much diverge. This suggests that the NGCU-2 glass is also homogeneous.

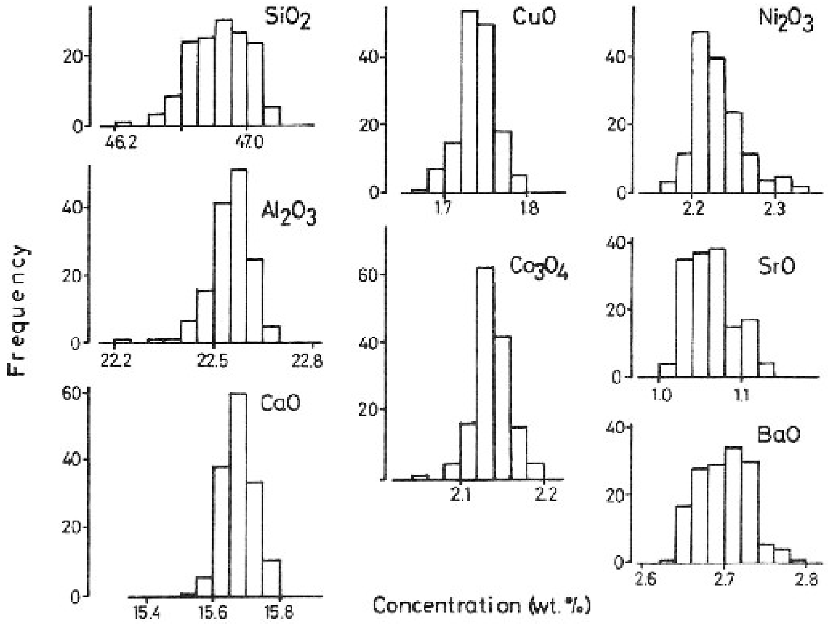

Fig. 4. Frequency distribution diagrams of the SiO_2, Al_2O_3, CaO, CuO, Co_3O_4, Ni_2O_3, SrO and BaO contents of 150 spot analyses on 30 different chips of the NGCU-2 glass.

Conclusion

The synthesized Cu-bearing Mg-Ca-Al silicate glasses, NGCU-1 and NGCU-2, are homogeneous. They do not show a significant compositional change described in terms of "Lineweaver mechanism" during electron beam bombardment and are acceptable as the microprobe standards. These silicate-based Cu-standards make it easy to apply the quantitative data-reduction procedures employed by most microprobe laboratories. The NGCU-1 and NGCU-2 glasses are available upon request.

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