The Io effect enables us to predict when most of the major radio events will occur, the duration and highest frequency of emission, and even the character of the emission spectrum. Quiet times can also be predicted. There is some evidence for year to year changes in the character of the emission and Io effect. Emission in 1964 was more patchy, weaker, and less frequent than in 1963 or 1962, and the Io effect (Fig. 1) was stronger in 1964. The significance of these changes has yet to be determined.

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10. I thank Prof. James W. Warwick for his suggestions, advice, and discussion; the High Altitude Observatory, National Center for Atmospheric Research, for use of the CDC 3600 computer and use of the records from the radio observatory; and the NSF for partial support of the project.

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Phase Relations in the System $Na_2Si_2O_5$–SiO_2

Abstract. *A new compound, $Na_6Si_8O_{19}$, is shown to be a thermodynamically stable phase in the Na_2O–SiO_2 system at 1 atmosphere. The new compound melts incongruently to SiO_2 (quartz) and liquid at 808° ± 2°C, and it disproportionates to $\beta Na_2Si_2O_5$ and quartz at 700° ± 10°C.*

The Na_2O–SiO_2 system has been studied by Kracek (*1*) who found $Na_2Si_2O_5$ as the only crystalline phase coexisting stably with quartz (SiO_2). Because of the thoroughness of this study it has usually been accepted as definitive. However, another silica-rich phase, $Na_2Si_3O_7$, has been reported (*2*). It was obtained by prolonged crystallization of a Na_2O–SiO_2 glass containing 75 percent SiO_2 (all percentages are mol percent). The reported x-ray powder diffraction data are certainly sufficient to establish that the mixture is distinctly different from any of the known polymorphs of SiO_2 and $Na_2Si_2O_5$. However, no proof of its formula or thermodynamic stability can be adduced from the data.

In our study, a compound which fitted Matveev's description (*2*) was readily prepared by devitrification of Na_2O–SiO_2 glasses containing 75 percent SiO_2. A few representative runs are shown in Table 1. Our glasses, like Kracek's, were prepared from reagent-grade laboratory chemicals, fused several times in platinum crucibles and checked for homogeneity. If random samples taken from a given preparation had a constant refractive index (± 0.001), the preparation was accepted as homogeneous. The composition of homogeneous glasses was checked by comparison of their refractive indexes with the values given in a critical compilation (*3*). The composition of crystalline starting materials was checked by chemical analysis for sodium as well as by fusing portions to a glass and measuring their refractive indexes. The two independent means of checking the composition agreed to within 0.5 percent Na_2O of the Na_2O composition stated in Table 1.

Small samples of the glasses and crystalline starting materials were crystallized in controlled temperature furnaces for periods ranging from several hours to 30 days (Table 1). At temperatures just below the solidus, the crystalline starting materials reacted rapidly and completely, giving relatively coarse-grained crystalline aggregates. Petrographic and x-ray powder diffraction examination showed that glass starting materials gave persistent metastable phase assemblages; $Na_6Si_8O_{19}$ was only one of the crystalline products encountered. However, crystalline starting materials containing 73 percent SiO_2 yielded a single homogeneous crystalline phase. Crystalline starting materials containing 75 percent SiO_2 gave considerable quartz as a second crystalline phase; those containing 72 percent SiO_2 gave a small amount of sodium disilicate ($Na_2Si_2O_5$) as a second crystalline phase. This fixes the composition of the phase as approximately 73.0 ± 1 percent SiO_2 and suggests that the phase must have a virtually constant composition in the temperature range 780 to 800°C. Matveev's proposed $Na_2Si_3O_7$ formula (75 percent SiO_2) is thus incorrect.

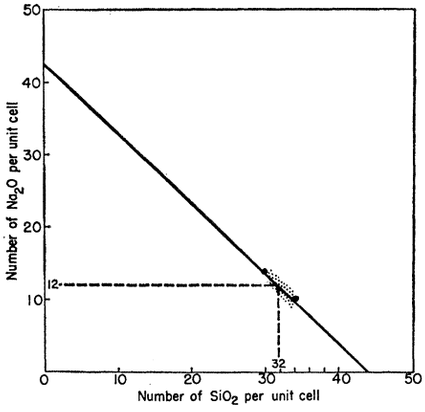

Fig. 1. Unit-cell contents of some hypothetical sodium silicates having a density of 2.50 and a unit-cell volume of 1768Å^3. The stippled area is bounded top and bottom by limits representing a possible error in the density of +0.05 and −0.05, respectively. Cell contents which are consistent with space group requirements and also lie in the stippled area include the $12Na_2O \cdot 32SiO_2$ formula whose intercepts are shown by dashed lines and two other compositions shown by solid dots. These have as intercepts $14Na_2O \cdot 30SiO_2$ and $10Na_2O \cdot 34SiO_2$ and have SiO_2 contents of ~ 68 and ~ 77 percent respectively. The $12Na_2O \cdot 32SiO_2$ formula is thus the only ratio fitting all the data (see text for discussion).

The formula was determined more exactly as follows. Single crystals were grown by cooling a 72.5 percent SiO_2 liquid through the interval between liquidus and solidus. Comparison of

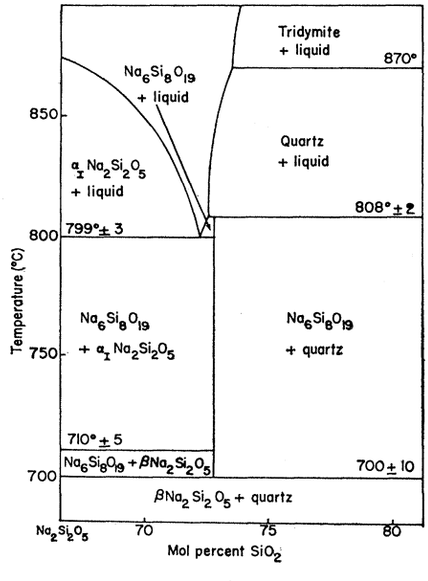

Fig. 2. A portion of the equilibrium phase diagram for the system $Na_2Si_2O_5$–SiO_2, showing a stability field of the $Na_6Si_8O_{19}$ phase. Liquidus data for runs that do not appear in Table 1 are taken mainly from Kracek (*1*).

Table 1. Critical quenching runs in the system $Na_2Si_2O_5$–SiO_2.

Comp. (% SiO_2)*	Time (hr)	Temp. (°C)	Phases present
Starting material: $\alpha Na_2Si_2O_5$+quartz			
72.0	24	796	$\alpha Na_2Si_2O_5$+$Na_6Si_8O_{19}$
72.0	24	802	$\alpha Na_2Si_2O_5$+liquid
72.0	30	813	$\alpha Na_2Si_2O_5$+liquid
72.0	24	818	Liquid
73.0	24	796	$Na_6Si_8O_{19}$
73.0	24	802	$Na_6Si_8O_{19}$+liquid
73.0	144	806	$Na_6Si_8O_{19}$+liquid
73.0	44	808	$Na_6Si_8O_{19}$+quartz +liquid
73.0	66	812	Quartz+liquid
73.0	22	843	Quartz+liquid
73.0	48	855	Liquid
75.0	24	802	$Na_6Si_8O_{19}$+quartz
75.0	30	813	Quartz+liquid
77.5	24	802	$Na_6Si_8O_{19}$+quartz
77.5	30	813	Quartz+liquid
Starting material: Na_2CO_3+quartz			
73.0	69	760	$Na_6Si_8O_{19}$
Starting material: glass			
73.0	18	800	Glass+$\alpha Na_2Si_2O_5$
73.0	200	800	Glass+$Na_6Si_8O_{19}$
73.0	23	818	Liquid
73.0	69	760	$\alpha Na_2Si_2O_5$+$Na_6Si_8O_{19}$ +cristobalite

* Mole percent.

single-crystal rotation photographs with powder patterns of various homogeneous preparations, showed that all single-crystal reflections were matched, both in position and intensity, by powder arcs. These photographs were taken on the same camera to facilitate the comparison. X-ray rotation and Weissenberg photographs showed that the unit cell had a volume of 1768Å^3. The correct formula must fill this cell volume to give the observed density of 2.48. Figure 1 shows a plot of all Na_2O/SiO_2 ratios fulfilling this condition. Of course, we must also consider the chemical evidence from direct-heating studies, as well as the space-group symmetry requirement, namely, that the number of atoms of each kind in the unit cell be an *even* integer.

These requirements give $Na_{24}Si_{32}O_{76}$ as the most probable formula. This formula gives a calculated density of 2.50 and a calculated composition of 72.7 percent SiO_2. However, because of experimental error in determining the cell volume and especially the density, any possible combination within the stippled quadrilateral (Fig. 1), should be considered. Some possibilities, for example $Na_{20}Si_{34}O_{78}$ or $Na_{28}Si_{30}O_{74}$, have the right density, but lie outside the limits of error of the composition established by heating studies.

As a further independent check on the density, the atomic refractivity values (R) were first calculated for Na and O, on the assumption that Si can be taken as zero. This assumption has been shown to be correct for the low-density silica forms and the calcium silicates (*5*). The calculations were made with the Lorentz-Lorenz equation

$$R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{D}$$

(where n is the mean refractive index, M is the formula weight, and D is density) and the mean refractive index and density of the known anhydrous sodium silicates, quartz and cristobalite. Values of R for Na and O are uniformly about 1.6 and 3.7 respectively. With these R values, the observed mean refractive index 1.503 and the $Na_{24}Si_{32}O_{76}$ cell contents, the calculated density is 2.47 ± 0.02.

The properties of $Na_6Si_8O_{19}$ may be summarized as follows. It is monoclinic, geometrically orthorhombic: space group No. 14; C_{2h}^5–$P2_1/c$; a = 4.90 ± 0.02 Å; b = 23.4 ± 0.1 Å; c = 15.4 ± 0.1 Å; β = 90°0′. The observed pycnometric density is 2.47_8 g/cm^3; the "sink-float" density is greater than 2.47_5 and less than 2.49_0. The density calculated for unit-cell contents $Na_{24}Si_{32}O_{76}$ (four formula units per cell) is 2.50. The crystals grow as elongated laths or needles and are optically biaxial with inclined extinction. The mean refractive index (sodium-D illumination) is 1.503, and the birefringence is low (~ 0.01). X-ray powder diffraction data are given in Table 3.

Comparison of the x-ray powder data and optical properties shows that $Na_6Si_8O_{19}$ is identical with Matveev's reported "$Na_2O \cdot 3SiO_2$" compound (*2*); $Na_6Si_8O_{19}$ may also be the phase reported by Schairer and Yoder as "phase W" (*4*).

Table 3. X-ray powder diffraction data for $Na_6Si_8O_{19}$.

I*	dÅ†	I	dÅ
vw‡	11.63	m	3.33
vw	10.70	mw	3.06
w	7.66	mw	2.98
vw	7.14	w	2.82
vw	6.44	w	2.72
w	5.46	vw	2.52
w	4.97	s	2.45
w	4.69	vw	2.34
w	4.47	w	2.27
vw	4.28	w	2.18
vw	4.24	m	2.11
m	4.12	w	2.05
m	3.83	mw	1.99
m	3.63	mw	1.93
m	3.44	w	1.870
vw	3.37	w/d	1.739

* Intensities (I) estimated from 6-cm films. † d-Spacings taken from a diffractometer trace, CuKα radiation, scanning speed ½°; 2θ/minute. Diffractometer calibrated with an external Si standard. Only the range of 2θ (Cu) 0°–60° is tabulated (*7*). ‡ w, weak; m, medium; s, strong; v, very; d, diffuse.

The $Na_6Si_8O_{19}$ phase can be prepared from a wide variety of starting materials. At temperatures between 750° and 800°C, appropriate mechanical mixtures of ($Na_2Si_2O_5$ + quartz) or (Na_2CO_3 + quartz) react readily to form $Na_6Si_8O_{19}$ (Table 1). These data indicate that the $Na_6Si_8O_{19}$ is thermodynamically stable. Quenching experiments indicate that at the upper limit of stability (808° ± 2°C), it dissociates sluggishly to quartz and liquid. The $Na_6Si_8O_{19}$ phase forms readily from glasses at temperatures as low as ~ 660°C and once formed persists in runs of up to 30 days' duration in air of ambient humidity. However, at moderate water vapor pressures (20–70 bars) the equilibrium:

$$Na_6Si_8O_{19} = 3Na_2Si_2O_5 + 2SiO_2$$

is readily reversible at 700° ± 10°C with either glass, $Na_6Si_8O_{19}$ or ($3Na_2Si_2O_5$ + $2SiO_2$) as starting materials; see Table 2.

The hydrothermal runs were made in open gold-foil envelopes. Slight leaching of Na_2O occurred during the runs. This was indicated by finding quartz as an exotic phase after reaction of the 73 percent SiO_2 mixture in the stability region of the $Na_6Si_8O_{19}$ phase. The quartz was identified optically and by x-ray powder diffraction. The relative quantity of quartz was estimated from the appearance of these x-ray powder patterns, compared with those obtained

Table 2. Critical hydrothermal runs in the system $Na_2Si_2O_5$–SiO_2.

Initial comp. (% SiO_2)	Starting material	Time (hr)	Temp. (°C)	Pressure (bar)	Crystalline phases
73.0	$Na_6Si_8O_{19}$	48	690	71	Quartz+$\beta Na_2Si_2O_5$
73.0	$Na_6Si_8O_{19}$	48	710	71	Quartz+$Na_6Si_8O_{19}$
75.0	Quartz+$\alpha Na_2Si_2O_5$	144	680	50	Quartz+$\beta Na_2Si_2O_5$
75.0	Quartz+$\alpha Na_2Si_2O_5$	168	715	54	$Na_6Si_8O_{19}$+trace quartz
76.5	Quartz+$\alpha Na_2Si_2O_5$	48	710	57	$Na_6Si_8O_{19}$+quartz
76.5	Glass	48	710	48	$Na_6Si_8O_{19}$+trace quartz
76.5	Glass	48	655	36	Quartz+trace $\beta Na_2Si_2O_5$

from mechanical mixtures containing known proportions of crystalline sodium silicates and quartz. Three to four percent quartz was readily detected. The magnitude of the leaching effect was thus estimated as being a 2 to 3 percent increase in silica content. A chemical analysis of the solid products of hydrothermal runs would not be meaningful; during the quenching step a hydrous glass was deposited around the crystalline products.

The hydrothermal runs were used only to fix the lower stability limit of the $Na_6Si_8O_{19}$ phase; this lower stability limit is unaffected by the presence of either excess $Na_2Si_2O_5$ or SiO_2.

These observations on the stability of the $Na_6Si_8O_{19}$ phase have been used to revise the phase diagram for the $Na_2Si_2O_5$–SiO_2 system (Fig. 2).

Differential thermal analysis of a crystalline $Na_6Si_8O_{19}$ sample shows no heat effects between room temperature and its melting point. The apparatus used could readily detect heat effects of 1 calorie per gram. There is, however, evidence that 72.7 percent SiO_2 glasses, devitrified at low temperature ($\sim$ 650°C or less), yield a metastable phase related to $Na_6Si_8O_{19}$ in structure and probably identical in composition.

The lower stability limit of the $Na_6Si_8O_{19}$ phase and its failure to persist metastably in the presence of H_2O, help explain why it has not been encountered in studies of the Na_2O–SiO_2–H_2O system (*6*). Such studies have covered only the temperature range where $Na_6Si_8O_{19}$ is unstable. We have no explanation of Kracek's failure to encounter this phase, except that possibly he depended on optical identification of the phases present: the gross optical properties—morphology and birefringence—of $Na_2Si_2O_5$ and $Na_6Si_8O_{19}$ are similar.

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19 March 1965

Specificity of Macroglobulin Antibody Synthesized by the Normal Human Fetus

Abstract. *The umbilical cord blood of 47 out of 54 normal human infants contains hemagglutinating activity directed toward cells coated with a type-L Bence-Jones protein. This hemagglutinating material, in some instances, is present in cord blood in the absence of such activity in the maternal blood. Ultracentrifugation of cord serum in a sucrose gradient shows that the activity is associated with the macroglobulin fractions.*

The normal human newborn has as its major circulating immunoglobulin γG-globulin transferred from the mother's circulation (*1*). Since γM-globulin apparently cannot be transferred across the placental barrier (*2*), the small amount of γM-globulin present in the normal human fetus at birth is thought to be of fetal origin. There is no direct evidence for antenatal synthesis of γG- or γA-globulins under normal circumstances.

No antibody specificity has as yet been detected in the γM-globulins of normal human newborn. I now report the presence of hemagglutinating activity in 47 of 54 serums obtained from the cord blood of apparently healthy human infants. Instances of the absence of such activity in the maternal serum when it is present in the infant strongly suggest the fetal origin of this circulating macroglobulin.

Serum from umbilical cord blood obtained at the time of delivery was examined together with the mother's serum obtained within 3 days thereafter. All mothers and their infants were entirely normal at the time of birth and in the immediate postpartum period.

Sheep erythrocytes treated with tannic acid were exposed to a solution of Bence-Jones protein (1 mg/ml), type L, isolated by gel-filtration chromatography from the urine of a patient having multiple myeloma (*3*). The protein solution was heated at 56°C for 15 minutes before being used for the coating procedure as described (*3*). The presence of protein as a cell coating was confirmed by agglutination of the cells in dilutions of rabbit antiserum to the L-polypeptide chain obtained from pooled normal γG-globulins (*4*).

Dilutions (Fig. 1) of the paired cord and maternal serums were examined with the use of cells coated with Bence-Jones protein, type L, No. 46. In three instances no hemagglutinating activity was detected in either cord or maternal serum in 1:20 dilution. In 23 instances the $\log_2$ titer of the maternal serum was equal to or greater than that of the corresponding cord serum. In 28 instances the titer of the cord serum was greater than that of the corresponding maternal serum, and in 14 of these cord-maternal pairs no hemagglutinating activity was detected in the maternal serum when there was demonstrable activity in the cord serum. Hemagglutinating substances with specificity for cells coated with type-K Bence-Jones proteins have been detected in all the maternal serums but in only three cord serums.

Previous studies of adult-human serum having hemagglutinating activity for sheep erythrocytes coated with Bence-Jones proteins revealed that the active proteins reside in the macroglobulin fraction as measured in serum fractions obtained after ultracentrifuga-

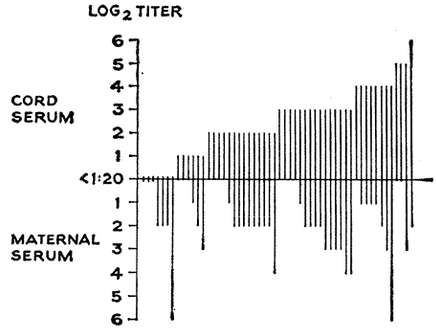

Fig. 1. $\log_2$ titers of umbilical cord serums and corresponding maternal serums expressed as bars above and below the initial 1-in-20 dilution. Cells coated with type-L Bence-Jones protein.

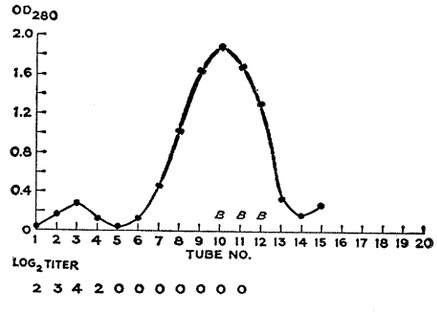

Fig. 2. Distribution of hemagglutinating activity in fractions obtained by centrifugation of cord serum No. 26 at 35,000 rev/min for 18 hours through a sucrose gradient. *B* designates fractions containing serum albumin.