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SILICON HALIDE-ALKALI METAL FLAMES AS A SOURCE OF SOLAR GRADE SILICON

Fourth Quarterly Report, March 1–May 31, 1978

By
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FOURTH QUARTERLY REPORT

D.B. OLSON AND W.J. MILLER

JUNE 1978

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Approved by
Hartwell F. Calcote
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FOREWORD AND ACKNOWLEDGMENTS

This is the fourth quarterly progress report on a program which began 17 May 1977; it covers the period 1 March 1978 through 31 May 1978.

Major contributions to the experimental effort on the program during this report period were made by G. Rolland, L. Koenig, and E.J. Louis.

ABSTRACT

This program is designed to demonstrate the feasibility of using alkali metal-silicon halide diffusion flames in a process for producing large quantities of solar cell grade silicon at low cost.

During this quarter we have completed $Na + SiCl_4$ flow tube experiments under a variety of conditions of pressure, reactor temperature, and flow velocity. Comparative experiments using 300 K Ar and 1000 K H_2/Ar diluents were performed with few differences in deposition rates or product characteristics found. Silicon from both sets of experiments was found to contain small amounts of Fe and other metal impurities.

A $Na + SiF_4$ experiment, run in an unheated reactor tube, was found to produce a large fraction of Na_2SiF_6, with only a small yield of Si.

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I. INTRODUCTION

The object of this program is to determine the feasibility of using continuous high-temperature diffusion flames of alkali metals and silicon halides to produce silicon in large quantities and of suitable purity for use in the production of photovoltaic solar cells. Thermodynamic calculations predict[1] that at the high adiabatic temperatures of these flames the alkali salt will be in the vapor phase while the silicon will be either liquid or solid. An industrial process is envisioned which takes advantage of this difference in physical state of the two reaction products to allow their efficient and continuous separation.

In the initial phase of this program[2,3] we established low pressure diffusion flames of these vapor-phase reagents in a simple opposed jet configuration. These experiments demonstrated that flames of Na or K with $SiCl_4$, $SiHCl_3$, and SiF_4 are stable and hypergolic, giving a solid reaction product which was deposited onto the walls of the reaction chamber. Samples of this solid were found to be comprised of very small (< 1 μm) particles. Washing of these samples with slightly acidic water removed the alkali salt, which comprises ≈ 90% of the weight of the samples, and left a brown powder. Analysis of this washed product showed it to be silicon.

In the second phase of the program[2,3] a flow tube apparatus was built in which an inert gas flow could be superimposed onto the alkali metal-silicon halide reaction producing a net flow of the products. In this manner it may be possible to separate various species nucleating and depositing onto the reactor walls at different rates. This experimental apparatus is also designed to allow experiments to be performed which closely simulate the conditions of the process proposed by the Westinghouse Corporation[4] which uses an arc-heated H_2/Ar stream to supply the enthalpy necessary to vaporize liquid sodium reagent and to produce a very hot, $T \approx 2400$ K, reaction environment. Our simulation experiments using vapor-phase reagents require only a moderate amount of preheating of the H_2/Ar and $SiCl_4$ to achieve an equivalent flame temperature.

During this quarter we have (i) continued to refine the flow tube apparatus; (ii) run approximately thirty flow tube experiments on the Na + $SiCl_4$ reaction under various conditions and in several different diameter flow tubes; (iii) run the first Na + SiF_4 experiment in the flow tube; and (iv) analyzed samples of Na + $SiCl_4$ and Na + SiF_4 reaction product using several techniques.

II. TECHNICAL DISCUSSION

A. APPARATUS MODIFICATIONS

Several modifications have been made to the tubular flow reactor although the overall configuration remains as shown in Fig. 4 of Ref. 3. The annular nozzle for $SiCl_4$ injection has been installed as a replacement for the ring injector. The inlet flange assembly is now as shown in Fig. 4 of Ref. 2. Flames obtained using this configuration are more compact and more intensely luminescent than those produced using the ring injector, indicating faster mixing of the reagents. A small heater for the $SiCl_4$ (or other silicon halide) vapor has also been added. This is simply a heated quartz tube in the flow line between the halide vaporizer and the reactor, with a thermocouple at its exit. A stainless steel tube was first used but the metal was rapidly attacked by the hot $SiCl_4$. The quartz shows no signs of reaction with the $SiCl_4$ and no decomposition products are found in the exit tube. This heater allows some flexibility in the temperature to which the H_2/Ar stream must be heated in experiments designed to simulate the Westinghouse process. The polyatomic $SiCl_4$ (and other silicon halides as well) has a considerably higher heat capacity than a H_2/Ar mixture, so higher input enthalpies can be achieved by rather modest preheating of this reagent stream. For example, the ratio $Cp(SiCl_4)/Cp(4H_2/Ar)$ at 500 K is 3.5, thus requiring heating of the $SiCl_4$ only 100 K to provide additional reaction zone enthalpy equivalent to heating the H_2/Ar 350 K.

Several different inner reaction tubes, both heated and unheated, were used during this reporting period. Chromel A resistance wire was wound around the outside of the tubing to form the heaters. In addition to the experiments with 6.4 cm i.d. Pyrex tube discussed in our last report,[3] we have used 6.0 and 2.1 cm i.d. quartz tubes and a 2.5 cm i.d. alumina tube.

We have begun using an inert atmosphere dry box for handling the sodium. Reducing the presence of small amounts of oxygen in the alkali vaporizer seems to greatly diminish problems associated with the corrosion of materials of construction by alkali metal vapor. We are currently separating the metal from its oxide coating by decanting it as a liquid. The oxide adheres to the container allowing the clean sodium to be poured into the vaporizer. More refined versions of this procedure may be developed at some future time.

B. FLOW REACTOR EXPERIMENTS

Over thirty Na + $SiCl_4$ experiments were run during this reporting period under a variety of reaction conditions. The first group of experiments was run under conditions similar to those of the Westinghouse process. Heated H_2/Ar diluent was used to increase the flame temperature to about 2400 K. Reactor pressures and linear flow velocities were relatively low at ≈ 0.1 to 0.25 atm and 0.5-2 m s^{-1}, respectively. An unheated 6.0 cm i.d. quartz tube was used. These conditions result in rapid cooling of the reaction products and the products were observed to nucleate and deposit rapidly onto the reactor walls. Samples of this product were found (as in prior experiments) to be composed of very fine particles (< 1 μm). If the two condensed products deposit in their stoichiometric 4NaCl + Si ratio, the samples would be 89.3% salt and 10.7% silicon by weight. Since the salt is easily removed by washing with slightly acidic (HCl) water, an investigation was made to see if samples taken from different parts of the reaction vessel contained higher silicon fractions. Samples taken from the flame region of the reactor (the first 20 cm of the tube) were found to be 50% richer in silicon than stoichiometric, with insoluble fractions of 16-22%. Samples taken from the downstream portion of the reactor were found to be 10-12% insoluble. Thus we see that in these experiments, which appear to be characterized by rapid nucleation of both products, silicon is apparently depositing onto the walls faster than the salt. Samples of the washed product from these experiments were subjected to impurity analysis (see Section II.C).

The second series of experiments was performed in this same 6.0 cm quartz tube heated to approximately 900 K prior to starting the reaction. The flame exothermicity further heats the tube walls in the reaction zone. Two experiments were performed with H_2/Ar diluent at approximately 1000 K and two with 300 K pure Ar diluent, both sets at volume flow rates of 50 STP cm^3 s^{-1} (linear flow velocities ≈ 70 cm s^{-1}). Another run was made with hot H_2/Ar at half the diluent flow rate. In these experiments most of the product collected in the first half of the 1 m long quartz tube. Specifically, in several runs an average of 76% of the solid was in the upstream half of the tube, 6% in the downstream half, and 18% collected on the particle filter in the line to the vacuum pump. The particle size of the material from the filter was smallest and was found to be slightly rich in salt content. Little difference was noted in solid product deposition or character between the experiments using the hot

H_2/Ar and cold Ar diluent. The flame, however, is less luminescent when H_2 is present in the diluent. The reason for this difference is not understood at the present time. Samples of the washed product from these experiments were also analyzed for impurities (see Section II.C).

To increase the linear flow velocity and reactor wall temperature we also used a quartz tube with 2.1 cm diam. Flow velocities were increased by a factor of eight and much higher wall temperatures were achieved. The NaCl/Si mixture was fused to the reactor walls, demonstrating that temperatures in excess of the melting point of salt (1074 K) were achieved. Following these experiments the small quartz tube was brittle, cracked easily, and it was impossible to separate the fused product from the reactor walls without destroying the tube. Other tube materials or better temperature control along the pipe are needed for these high temperature experiments. Several experiments were performed using a high purity alumina tube of 2.5 cm i.d. which will withstand the temperature necessary in this work. Alumina is not, however, expected to be an acceptable material for the reactor walls, since the sodium does react with this material and Al contamination of the silicon would be expected. Very high wall temperatures were achieved in these experiments, estimated to be 1300-1500 K. Almost all of the solid product was found in the 10 cm downstream from the flame zone. This material was dark brown, crystalline, and covered most of the cross sectional area of the tube. Large fused salt crystals were found at the downstream end of the deposit.

A Na + SiF_4 experiment was run in the 6.0 cm i.d. unheated tubular flow reactor using Ar diluent at ≈ 1000 K. As was observed in our earlier experiments[3] in the opposed-jet reactor, this flame was not as intensely chemiluminescent as the $SiCl_4$ flames. Large quantities of solid product, which are similar in appearance to the product of $SiCl_4$ reactions, were deposited onto the reactor walls. The washed product was dark brown, in contrast to the tan color of the product from our earlier SiF_4 experiments. Weight-loss measurements showed a large insoluble fraction near the flame zone, with 18.2% insoluble compared to 6.5% remaining after washing of the downstream product. The stoichiometric product of this reaction would be 14.3% silicon. However, a possible interference to the production of silicon exists[5,6] due to the reaction $SiF_4 + 2NaF \rightleftarrows Na_2SiF_6$, this product also being insoluble in water. To test whether our insoluble product was Si or a mixture of Si and Na_2SiF_6, we heated a sample to 1300 K under vacuum. At this temperature the equilibrium vapor pressure of SiF_4 would be greater than one atmosphere[6] and the Na_2SiF_6 would be completely decomposed. The residue was found to be 26% insoluble, the remainder presumably being NaF. The amount of silicon in the original product was therefore quite small, less than 18.2% x 26% or 4.7%. This Na + SiF_4 experiment was run with an unheated, uninsulated quartz tube, giving very rapid quenching of products. Higher reaction temperature and wall temperature should shift the equilibrium of the SiF_4 + NaF reaction away from the direction of Na_2SiF_6 production. Further experiments are needed to see if larger yields of silicon can be obtained.

C. PRODUCT ANALYSES

Scanning electron microscope (SEM) photographs of unwashed and washed samples of Na + $SiCl_4$ flow tube experiments have been obtained and are shown in Figs. 1 and 2, respectively. The unwashed samples contain a larger portion of submicron "dust" along with larger (2-50 μm) particles. The larger entities appear to be rather loosely adhering agglomerates of small particles, with a highly textured surface. Similar SEM photographs of the washed product show particles in the 2- 40 μm range, with none of the loose "dust" visible. The washed particles appear to be more crystalline in character with smoother surfaces and more sharply defined edges. Apparently in the unwashed sample these Si particles are covered by a coating of small particles which are soluble in water. The small particles and "dust" are therefore tentatively identified as NaCl while the silicon appears to be present in the larger sizes.

Impurity analysis of silicon samples by X-ray fluorescence has proven to be unreliable and alternate methods are being evaluated. Eight samples from Na + $SiCl_4$ experiments and one from the Na + SiF_4 experiment were sent to a commercial laboratory for analysis by emission spectroscopy. Although this technique is not extremely sensitive, it offers a relatively simple and inexpensive analysis for a wide variety of possible impurities. After the impurity level of our silicon is reduced below the threshold detection level of this method, we will proceed to other more sensitive techniques including neutron activation analysis at Lawrence Livermore Labs. Silicon samples with precisely known amounts of impurities were obtained commercially to standardize the measurements and calibrate the results. Samples were tested for thirty-one elements, and only nine elements were detected. Several other impurities of special interest in silicon for solar cell applications (boron, titanium, and zirconium, for example) were not detected at threshold levels of 10 ppm. Table I shows the results of these analyses. The product is confirmed to be silicon with an average of 0.016% Na (as NaCl). No special efforts were made in the washing process to be thorough in removing the salt. Sample #9 however contains Na as a principal component, lending additional support to the suggestion that large amounts of Na_2SiF_6 are present in this particular Na + SiF_4 reaction product. Samples #1 and #2, from an early experiment in an unheated quartz tube, contain considerable amounts of impurities from stainless steel (Fe, Cr, and Ni). The other samples show a much reduced level (2 ± 1 ppm) of Fe, with Cr and Ni not detected. Possibly Sample #1 was contaminated in the laboratory during handling. Sample #9 from the experiment in the alumina tube shows 5 ppm of Al, demonstrating the unsuitability of this tube material for high purity work. Considerable traces of Cu and Mg are present from unknown sources (the Mg was detected but the actual concentration not determined).

X-ray diffraction studies were performed during this reporting period on several samples of washed product to determine whether the silicon produced in these flames has a crystal structure. Product from (i) two recent Na + $SiCl_4$ flow tube experiments, (ii) three opposed jet K + $SiCl_4$ experiments, and (iii) the Na + SiF_4 flow tube experiment were analysed. The diffraction results from (i) showed three peaks at angles of 28.4, 47.3, and 56.1 degrees corresponding well with standard angles for crystalline silicon of 28.44, 47.34, and 56.08 degrees. The relative peak intensities of 1.00/0.57/0.32 also compared closely with the standard 1.00/0.60/0.35 intensity ratios. No other significant peaks were observed; in particular the diffractions due to NaCl at 27.35, 31.69, and 45.45 degrees were not visible. Results from the opposed jet samples showed much less crystalline nature material; the diffractions were considerably weaker and broader. Microscopic examination of these samples showed them to be much less uniform in particle size and color. Many white crystals, presumed to be salt, were also observed. The last sample, that from the Na + SiF_4 reaction, showed a very different result. Ten relatively large peaks (and six smaller peaks) were observed, including the three due to silicon, but at reduced intensities about half that of sample type (i). The other peaks are due neither to NaCl or NaF and are presumed to be due to Na_2SiF_6.

III. CONCLUSIONS

Tubular flow experiments under various conditions of pressure, reactor temperature, and flow velocity have been performed using Na + $SiCl_4$ flames producing large samples of solid reaction product. Heat losses are such that rapid cooling of the flame products occurs and the silicon and salt appear to quickly nucleate and deposit onto the reactor walls. Slight enrichment of the silicon fraction over stoichiometric was found near the flame zone although the alkali salt still comprised $\approx$ 80% by weight of the product. Simple washing techniques reduce the salt content of the mixture by 3 to 4 orders of magnitude leaving 100-300 ppm NaCl in the silicon. Small amounts of iron and other metal impurities are found in the silicon when analyzed by emission spectroscopy. Experiments at higher reactor temperatures will require different tube materials than have been used to date.

The Na + SiF_4 experiment performed under conditions of rapid quenching of the products produced a large percentage of Na_2SiF_6 with only about a 30% yield of silicon. Further experiments are needed on this system to see what reaction temperatures are necessary to prevent the formation of Na_2SiF_6.

IV. PLANS

During the next quarter we plan to (i) continue experiments on the Na + $SiCl_4$ reaction with efforts directed toward attaining higher wall temperatures and operating at higher pressures, (ii) run further Na + SiF_4 experiments to determine how high the operating temperatures must be to prevent formation of Na_2SiF_6, and thus provide higher yields of silicon, and (iii) melt powdered silicon and silicon/salt samples in order to make resistivity measurements on the fused crystals as a simple indicator of product purity and separation.

V. NEW TECHNOLOGY

No reportable items of new technology have been identified.

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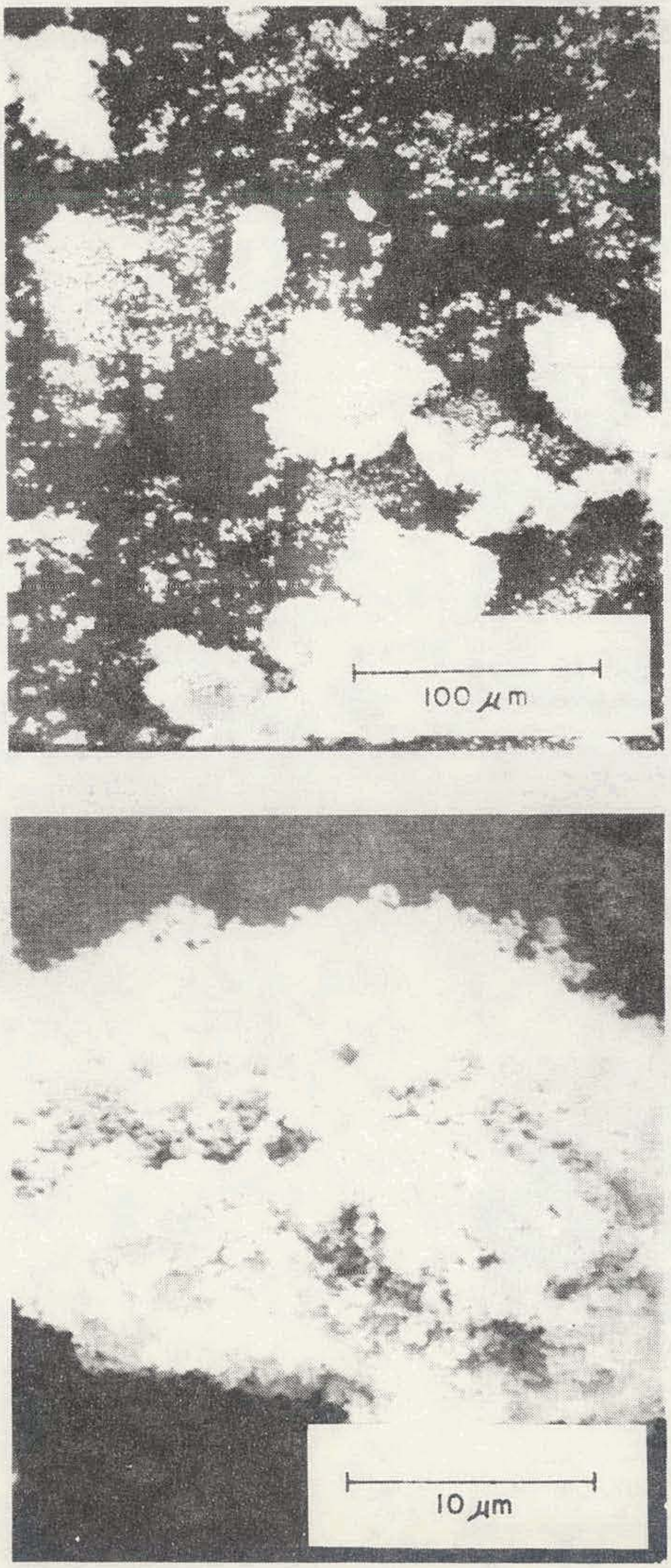

FIGURE 1

ELECTRON MICROSCOPE PHOTOGRAPHS
OF UNWASHED PRODUCT
(4NaCl + Si)

(Viewed at 45 degrees)

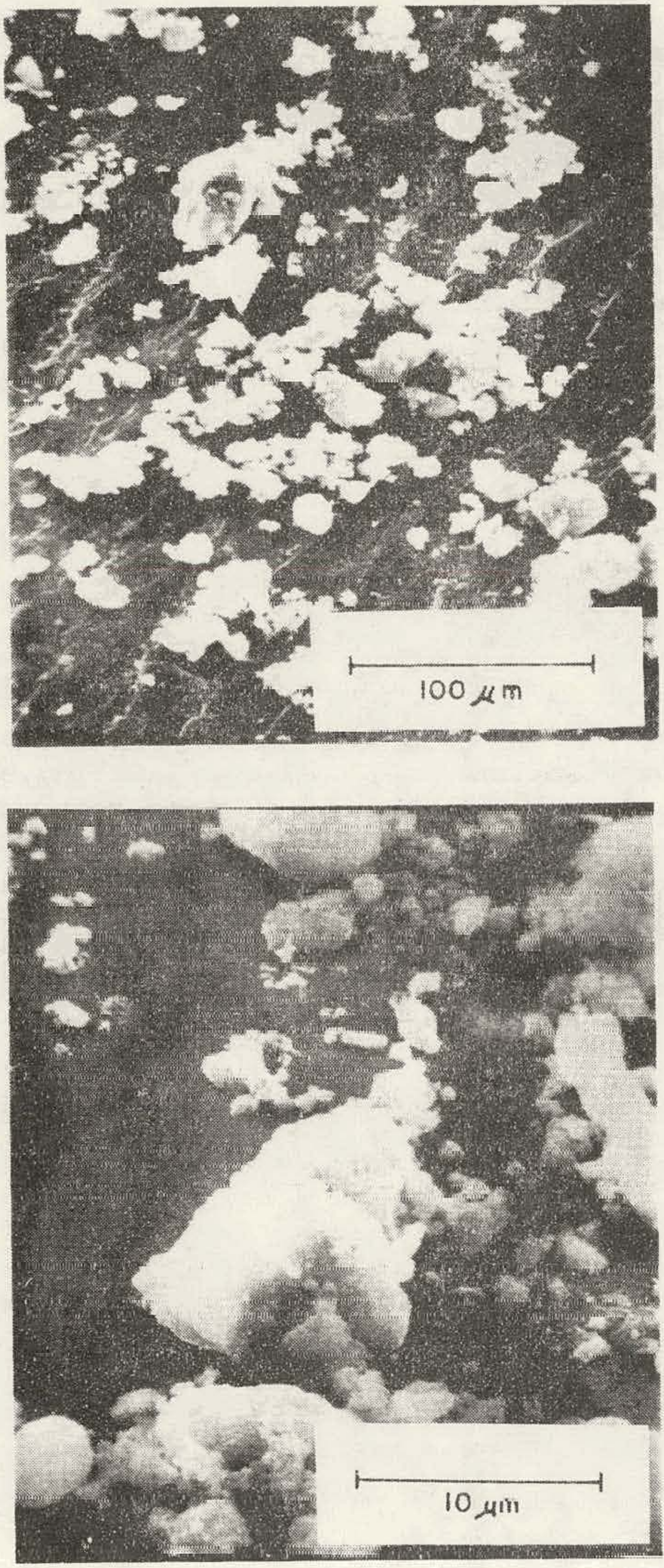

FIGURE 2

ELECTRON MICROSCOPE PHOTOGRAPHS
OF WASHED PRODUCT

(Viewed at 45 degrees)

TABLE I

SPECTROCHEMICAL ANALYSIS OF SILICON PRODUCED IN SODIUM-SILICON HALIDE FLAMES

Element	Concentration, ppm								
	Sample: 1	2	3	4	5	6	7	8	9
Si	P[a]	P	P	P	P	P	P	P	P
Na	100	200	350	200	150	100	90	90	P
Fe	150	5	3	3	2	2	–[b]	2	1
Cr	50	–	–	–	–	–	–	–	–
Ni	20	5	–	–	–	–	–	–	–
Al	< 1	< 1	–	–	–	–	–	5	–
Cu	10	10	1	4	2	2	2	5	1
Mg	< 1	< 1	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Ag	–	–	< 1	< 1	–	–	–	< 1	–

[a] P = principal component

[b] – = below threshold and not detected

Sample	Run No.	System	Reactor	Diluent	Volume Flow Rate (STP cm^3 s^{-1})	Remarks
1	15	$Na + SiCl_4$	6 cm unheated quartz tube	hot H_2/Ar	150	sample from flame zone
2	15	$Na + SiCl_4$	6 cm unheated quartz tube	hot H_2/Ar	150	sample from downstream tube walls
3	23	$Na + SiCl_4$	6 cm heated quartz tube, $T \approx 950$ K	hot H_2/Ar	50	
4	24	$Na + SiCl_4$	6 cm heated quartz tube, $T \approx 950$ K	hot H_2/Ar	50	
5	25	$Na + SiCl_4$	6 cm heated quartz tube, $T \approx 950$ K	300 K Ar	50	
6	26	$Na + SiCl_4$	6 cm heated quartz tube, $T \approx 950$ K	300 K Ar	50	
7	28	$Na + SiCl_4$	6 cm heated quartz tube, $T \approx 950$ K	hot H_2/Ar	25	
8	31	$Na + SiCl_4$	2.5 cm heated alumina tube, $T \approx 1400$ K	hot H_2/Ar	50	
9	18	$Na + SiF_4$	6 cm unheated quartz tube	hot Ar	75	probably contains Na_2SiF_6

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