UNITED STATES DEPARTMENT OF THE INTERIOR
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Uranium Mobility During Interaction of Rhyolitic Glass with Alkaline Solutions: Dissolution of Glass

By

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This report is preliminary and has not been edited or reviewed for conformity with U.S. Geological Survey standards and nomenclature.

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Abstract

This report concerns investigations designed to identify the important physical and chemical parameters influencing the rate of release of uranium from glass shards of rhyolitic air-fall ash. Oxidizing, silica undersaturated, alkaline solutions are eluted through a column of rhyolitic glass shards at a carefully controlled temperature, pressure, and flow rate. The solutions are monitored for the concentration of uranium and selected additional elements (Si, K, Li, F), and the glass is recovered and examined for physical and/or chemical evidence of attack. The flushing mode is designed to mimic leaching of glass shards by intermittent, near-surface waters with which the glass is not in equilibrium. Reported rates are applicable only to the experimental conditions (120°C, 7,000 psi), but it is assumed that the reaction mechanisms and the relative importance of rate-influencing parameters remain unchanged, at reduced temperature and pressure.

Results of the above experiment indicate that silica and uranium are released from glass shards at comparable rates, while lithium and potassium are released faster and flourine slower than either Si or U. Rates of release of silica and uranium correlate positively with the surface area of the shards. Rhyolitic shards release uranium at faster rates than rhyodacitic shards of comparable surface area. Changes in the shards resulting from experimental

treatment and observed in the original glass separates from an Oligocene ash (compared to a Pleistocene ash) include; surface pitting, increased surface area, devitrification rinds (<1 micron wide) and reduced lithium contents. Future investigations will study the effect of temperature, pressure, solution composition, and flow rate on the relative mobility of U, Si, Li, F, and K.

Introduction

The common close association of sedimentary uranium deposits with acidic, air-fall ash has generated much speculation that rhyolitic ashes, specifically the glassy components, are good sources of easily mobilized uranium. The following experimental study is an investigation of the rate of leaching of uranium from glass shards in rhyolitic ash. Previous studies that have attempted to identify uranium source rocks have used bulk chemical analyses of the uranium content of fresh and altered ash deposits, but the results of such analyses are difficult to interpret because of the lack of information on the capacity of various alteration products to incorporate uranium from solution. In this study, the experimental conditions were designed to minimize the effects of alteration products on solution composition. The results of this and subsequent studies will attempt to identify the important variables influencing rate of uranium release from ash and will monitor residual glass shards for physical and/or chemical changes indicative of prior extensive contact with groundwater. At present, the only reliable technique for directly measuring the likelihood of major uranium loss from glass is measurement of disequilibria amongst the short-lived daughters of the uranium decay series. Such measurements are laborious and only document major disturbances within the last 300,000 years (Rosholt, 1959).

Studies comparing the relative uranium contents of massive obsidian and coexisting unaltered felsite from rhyolite lavas and ash flows indicate that devitrified lavas are better uranium source rocks than massive glass (Rosholt and others, 1971; Zielinski and others, 1977). Except in the vicinity of volcanic centers, ash flows and lavas are volumetrically minor and the relative leachability of massive obsidian and fine-grained glass shards may be different enough to disqualify broad application of the above results. If mobilization of uranium is primarily by a mechanism requiring contact with groundwater, fine-grained porous glass of high surface area should react at much greater rates than large, relatively impermeable masses of obsidian. Field evidence for the rapid alteration of volcanic glass is the virtual absence of rhyolitic glass older than the Tertiary, the zeolitization of 10,000-20,000 years old rhyolitic ash deposited in alkaline lakes (Cook and Hay, 1965; Hay, 1963), and the argillation of volcanic ash within a period of 4,000 years in a tropical environment (Hay, 1960).

In the following study, well described samples of rhyolitic glass and a synthetic rhyodacitic glass are subjected to attact by aerated, alkaline solutions. Fresh solution is eluted through each sample at a controlled rate, temperature and pressure. Leach solutions are monitored for concentrations of dissolved uranium as well as some selected elements (Si, K, Li, F) chosen to compare and contrast with uranium. After the experiments, the glass shards are recovered and compared with splits of the original material. The design of this leaching experiment is intended to simulate near-surface intermittent washing of glassy ash by fresh waters with which it is not in equilibrium.

Experimental parameters represent a compromise between natural conditions and those which produce conveniently measured amounts of dissolved constituents. Reported concentrations of dissolved constituents and rates apply only to the reported experimental (120°C, 7,000 psi) non-equilibrium conditions. It is assumed that the reaction mechanisms and the relative importance of rate-influencing parameters remain unchanged at lower temperatures and pressures.

Apparatus

The experimental design is modelled after that developed by Morey and Fournier (1961). Leach solution is pumped from a reservoir by means of an air-driven plunger pump (figure 1). The solution passes a double-ball check valve, pressurized reservoir, and 5-micron line filter before entering one of four sample lines. Each sample line contains a single-ball check valve to prevent back flow, a pressure gauge, a sample chamber within an enclosing resistance furnace, an on-off valve, and regulating valve. During operation, solutions are kept at a constant pressure and temperature while flowing slowly past samples of glass shards. As solutions are collected from the regulating valve outlets the pump actuates to maintain pressure. Pressure is generally maintained within 500 psi of the desired level during pumping. Following sampling, each sample line is closed off from the rest of the system by on-off valves at each end.

Figure 1 - NEAR HERE

Temperature is measured by platinum-rhodium thermocouples inserted in wells in the sample holder and the furnaces are regulated by time-proportioning potentiometric temperature controllers. Temperature control is ± 2°C. The sample holders are placed in the "hot spots" of the furnaces where measured temperature gradients are <1°C/cm.

Temperature gradients within the sample holders during flow-through operation were not measured. Morey and Fournier found a transient gradient of 10°C which persisted only during the first minute of flow. Inside surfaces of the sample holders (figure 2) are plated with platinum on a gold intermediary layer to minimize possible contamination of the glass or leach solution during high temperature leaching. Stainless steel high pressure tubing (1/4-inch OD, 3/32-inch I.D.) contained in the heated area was not protected by plating and is the most likely source of contamination. Sealing of the sample chambers is obtained by pressure of ribbed pistons against copper washers. The glass shards are contained within the chamber (.9 x 10 cm) by filter discs of 15-micron opening supporting teflon filters of 5-micron opening. Mesh and filter paper are held in place by flanking copper washers.

Figure 2 - NEAR HERE

Starting Materials

Glass separates from two rhyolitic tuffs and a synthetically prepared glass were used for the experiments (Table 1). One sample line was left empty to act as a system blank.

Table 1 - NEAR HERE

1) Bandelier Tuff (Pleistocene) (65W129); 250-350 mesh glass separate from the Tsankawi Pummice Bed, (1.1 MY), Jemex Mtns., N.M., (Izett and others, 1972).

2) White River Formation (Oligocene) (WTR-SBI); 250-325 mesh glass separate from glassy tuff (32 MY), collected by the author in the Shirley Basin uranium district of Wyoming.

3) Nonhydrated, rhyodacitic synthetic glass (GSD); <325 mesh glass prepared as a spectrographic standard for the USGS by the Corning glass works and doped with 46 trace elements at $\approx$ 50 ppm concentration (Myers and others, 1976).

The solution chosen for the leaching experiments was 0.05M Na_2CO_3 + 0.05M $NaHCO_3$, pH 9.9 (25°C), aerated with purified air. Groundwaters in rhyolite tuffs are typically dominated by sodium and bicarbonate ions (Schoff and Moore, 1964; Harshman, 1972). The carbonate-bicarbonate mix acts as a pH buffer preventing the pH from rising to levels where U might precipitate as uranate (Clegg and Foley, 1958). Table 2 presents a comparison of some natural and industrial leaching solutions analogous to the experimental mix.

Table 2 - NEAR HERE

Experimental Procedure

Approximately 100-120 ml of leach solution were collected over a four hour period on weekdays. Flow rates during sampling were 0.5 ± .1 ml/minute. For a glass column of 10 cm and typical interstitial volume of 5.5 cm^3, one calculates a simulated groundwater flow of 4778 m/year. Daily samples were collected for the first six days of operation. Flow was then stopped and the ash samples were allowed to digest in leachate for a period of 46 days. After renewal of flow, daily samples were collected for three days, two-day collections were combined during a two-week period, and finally, pooled leaches for 5 days were combined during the last three weeks. Total duration of the experiment was 113 days and total volumes collected were 3700-3800 ml per ash sample. One ash (Bandelier #33, day 112) was sampled in 2 ml aliquots during collection of the first 20 ml drawn after overnight shutdown.

Temperature and pressure of the sample chambers were controlled at 120° ± 2°C and 7,000 ± 250 psi. The temperature and pressure chosen are closer to hydrothermal than weathering conditions but kinetic considerations require somewhat elevated temperatures. An upper limit of temperatures for this type of experiment should be $\approx$ 200°C since silica glass can recrystallize to quartz above this temperature. Minimum pressures for such experiments are approximately those which allow smooth flow of solution and prevent carbonate decomposition at the experimental temperatures.

Rough estimates of the Eh conditions within the reaction vessel (uncorrected for temperature and pressure) may be made by the observation that the copper washers used to maintain a tight seal of the sample chamber developed coatings of black cupric oxide. At pH = 9.9 (25°C) cupric oxide is stable in water at an Eh greater than 0 volts. Uranium (10^{-6}M) in a carbonate solution (.1M) of this Eh and pH (25°C) exists as a uranyl dicarbonate complex (Garrels and Christ, 1965, p. 225). Buffering Po_2 by reaction of H_2O with the stainless steel of the reaction vessel has not been observed at temperatures <700°C (Eugster and Wones, 1962).

Samples were collected and stored in acid-washed polyethylene bottles. Splits were taken within a few days of collection for analysis of U, Si, F, Li, and K. All analyses were generally completed within one month of collection. Splits of 5 ml were acidified with 6N HNO_3 to pH $\approx$ 2 and stored for possible future study.

After the experiment, the solid residues were removed from the bombs, washed with water and recovered on .45 micron millipore filters. A very fine dust of reddish precipitate believed to be a mixture of copper oxide (Cu_2O) and iron oxides originating from the copper washers and stainless steel was decanted during slurrying of the glass with water. Quantitative recovery of glass was not possible but fractional loss of major and minor components resulting from leaching could be calculated from analyses of the solutions (below).

Silica was measured in freshly collected leach solutions by the colorimetric, molybdate blue method following a fusion of the evaporated sample in sodium carbonate. The fusion procedure was added to insure detection of dissolved silica which may have been present in polymeric forms. While all solutions were clear, easily filterable, and free of measureable precipitates at the time of collection, filtration studies performed at subsequent intervals indicated growth of gelatinous silica precipitates which hindered filtrations and grew to macroscopic size after intervals of 1-3 weeks storage. Comparison of molybdate blue determinations performed with and without fusion verified the fact that silica was precipitating from solution.

In order to minimize the effect of possible coprecipitation of uranium with silica, uranium determinations were performed as quickly as possible. A fission track procedure modified from Reimer (1976) was utilized. A platelet of low uranium silica glass was submerged in an aliquot of the solution and a polyethylene vial containing solution and glass "detector" was submitted to the USGS TRIGA reactor for a neutron dose of $3.6 \times 10^{16} n/cm^2$. During irradiation, U^{235} in the sample undergoes fission and some fission fragments recoil from the solution into the glass detector causing structural defects which are made visible by subsequent etching of the recovered platelet in 50 percent HF for two minutes. The density of the developed "fission tracks" was counted using a microscope and compared to the density produced by a standard solution of uranium. The accuracy of the method was verified by fluorimetric determinations. The technique was especially useful in this study because of the small sample volumes required (0.5 ml). A fission track procedure using muscovite detectors mounted on polished grain mounts was used to observe uranium distribution in shards before and after leaching (see below).

Dissolved concentrations of lithium and potassium were determined by atomic absorption and fluorine by ion electrode measurements. The techniques provided accurate data from minimal sample volumes.

Analyses of the leached and original shards were performed by several techniques chosen to monitor both physical and chemical changes (Table 3). Polished grain mounts were prepared in order to study the grains by petrographic microscope, scanning electron microscope (SEM), and electron microprobe as well as to prepare fission track maps of U distribution. Splits of the glass shards collected before and after leaching were submitted for analysis of U and Th by a delayed neutron technique (Millard, 1976), F by ion electrode, and Li by atomic absorption. Other splits were submitted for X-ray diffraction analysis, size and shape analysis by automatic image analyzer, and surface area measurements by 4-point, nitrogen gas adsorption.

Table 3 - NEAR HERE

Results and Discussion

Leach Solutions

In general, the abundance of U, Si, K, Li, F in the leach solutions showed little day-to-day variation (Table 4).

Table 4 - NEAR HERE

This was expected since all variables influencing the rate and degree of solution in an open system (pressure, temperature, solid-liquid compositions, grain size, flow rate, solid/liquid ratio) were relatively constant for each sample during the leaching experiments. Exceptions producing anomalously high concentrations were 1) the first day of leaching during which surfaces may have been more reactive as a result of prior crushing and handling of the shards and/or more soluble because of extremely fine-grained particulates produced during crushing, 2) the first day after a 46 day shutdown during which time concentrations of dissolved species in the $\approx$ 5 ml of interstitial solution may have increased to much higher levels than obtained by shorter grain-solution contact times.

The latter case was studied during sampling of Bandelier #33 in which the interstitial volume in contact with ash for 20 hours was measured for Si and U (figure 3). After

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Figure 3 - NEAR HERE

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draining of $\approx$ 2 ml of dead volume present between the sample chamber and outlet valve, solution concentrations within the next 2-5 ml showed marked increases in Si and U. After tapping 10 ml of solution, concentrations dropped to levels characteristic of the steady-flow open-system leaching.

Enrichment factors of the interstitial solutions, defined as the calc* concentration interstitial solution/concentration of average leachate, were much greater for U ($\approx$ 10) than Si (4) implying that higher U/Si ratios result in ash leachate solutions approaching silica saturation. This phenomena will be investigated in a future study. During rapid flow leaching, the silica content of a solution is low, and the soluble silica and uranium are in the same ratio to their weight in the starting material (Table 4).

Enhanced removal of K and Li may result from rapid diffusional transport of these elements within glass. The result is a diffusion-depleted layer in advance of the dissolution-devitrification front (Csákvári and others, 1971; Boksay and others, 1967; Baucke, 1974).

*Interstitial volume may be calculated from the volume of the sample chamber ($\simeq$7.3 cm^3) and weight of ash sample (density = 2.3 g/cm^3). Weight of material in the interstitial solution is calculated from the amount contained in the first 14 ml of leachate corrected for the amount dissolved in [14-(interstitial volume)] milliliters. Concentration of this latter volume is assumed $\approx$ to the average values shown in Table 4.

Rate of fluorine loss may depend upon the nature of its incorporation in glass. Some component of fluorine may be present in fresh glass as easily leachable surficial coatings (Ellis and Mahon, 1967).

Investigation of the Solid Phases

Observation of polished mounts of original and leached shards under transmitted, reflected, and polarized light showed little evidence of change due to experimental treatment except for apparent enhancement of a thin (<1 μm) rim or dusty surface of devitrification observable under crossed polars. Likewise, observation of shard morphology with the scanning electron microscope did not allow accurate evaluation of surface changes. The original shards from tuff of the White River Formation were notable for the presence of many pitted surfaces believed to be the result of weathering (figure 4). After leaching in the experimental system the pits appeared to be more rounded and scoured around the edges.

Figure 4 - NEAR HERE

In order to more fully quantify physical changes in a population of small grains of various shapes and sizes, splits of shards were measured for average size (ϕ of 300 grains) and degree of roundness (area/perimeter^2 of 100 grains) with an automatic image analyzer. Results were expressed as a frequency distribution and statistical parameters such as the mean and std. deviation were calculated (Table 5). Results show no significant reduction in average size (ϕ increases) or degree of roundness (A/P^2 approaches .08) as a function of the leaching process. Perhaps major dissolution is confined to the smallest grains which are not efficiently measureable by image analysis. Grain size distribution varied from nearly Gaussian (Bandelier) to bimodal (White River).

Table 5 - NEAR HERE

More dramatic changes in surface area as measured by nitrogen gas absorption (Table 5) are a result of formation of the feathery, devitrified rims observed with the optical microscope. It is possible that the partially dissolved, devitrified rims could develop without producing significant changes in the average grain size as measured by the image analyzer. Precision of the surface area measurements was determined by replicate analysis to be ± 10 percent but accuracy is difficult to evaluate because of possible differences in surface areas available to nitrogen compared to water and lack of universally accepted surface area standards. Pitting and devitrification rims observed in White River Formation starting material is reflected by a higher surface area compared to calculated surface areas of spheres of the same density and average diameter.

While uranium concentrations of leachate showed no dramatic increases during the experiments, the relative amounts ultimately leached from the two natural rhyolitic glasses display a positive correlation with the starting surface area or estimated mean surface areas during the course of the experiment (Tables 4, 5)

A rhyolitic glass (Bandelier) leached under identical conditions and with approximately the same surface area as the rhyodacitic synthetic glass lost greater amounts of U and Si.

X-ray diffraction patterns of glass samples before and after leaching (Figure 5) show a variety of effects ranging from no change (GSD glass) to development of potassium feldspar. Although observed volumetric abundance of devitrification products was minor, surficial coatings of alteration products are preferentially detected by x-ray diffraction. The apparent reactivity of the natural samples may reflect the importance of solid phase bulk composition and/or the presence of seed crystals of potassium feldspar in the natural glasses. Crystallization of potassium feldspar at low pressure and temperature is favored in solutions of high $K^+:H^+$ activity ratios, high salinity and high silica activities (Hemley and Jones, 1964; Garrels and Howard, 1959; Orivlle, 1964).

Figure 5 - NEAR HERE

Values of the concentration of silica, Na^+, K^+, H^+, in collected leach solutions may be used with the phase diagrams developed by Hess (1966) to make rough estimates of the stable alteration products expected. At 25°C, pH = 10, the leachate solution composition corresponds to that in equilibrium with idealized phillipsite ($Na_{0.5}K_{0.5}AlSi_3O_8 \cdot H_2O$). However, the increased temperature of the experiments and likely elevated concentrations of silica (Figure 3) and potassium in interstitial leach solutions during system closure create conditions most favorable for potassium feldspar formation.

Comparison of data for the two rhyolite glass samples indicates uranium leachability (Table 4) does not correlate with the degree of development of potassium feldspar peak intensities. Comparison of relative peak heights is complicated by peak height variations caused by variable preferred orientations of crystals in the powder diffraction mount.

X-ray diffraction evidence of calcite precipitation during leaching of the high-calcium synthetic glass (Figure 5) reflects the low solubility of calcite in carbonate-rich leach solutions.

Attempts to directly measure chemical gradients produced within leached glass shards were generally unsuccessful. Fission track maps of uranium distribution in leached and unleached shards showed no discernable concentration variations. The resolution of the technique is limited by the length of the fission tracks (5 µm).

Chemical gradients involving major elements were tested with the electron microprobe (ARL, 15 KV, 10 NA). Chemical analyses of eight major elements were performed at ten random points within the center of a shard and at ten points within 5 µm of the rim. Mean, standard deviation, and variance were calculated for each group within the shard and 5 shards were investigated from a split of each glass sample. Analysis of variance showed that variance associated with experimental treatment was insignificant compared with elemental variability present in the original glasses. Potassium and sodium variability were generally greater than the other measured elements. Both Na and K are subject to ion exchange with groundwater during glass hydration (Aramaki and Lipman, 1965; Noble, 1967, Truesdell, 1966).

Bulk chemical analysis for minor elements (Table 6) indicated that elemental concentrations in the undissolved residue after experimental leaching were not markedly changed. The results are expected given the small amounts of dissolution, the apparent near congruent solution of Si and U, and the error in analytical measurement. The concentrations expected in the residuum may also be calculated from the data of Table 4 and generally are within the precision limits of the measurements on leached shards.

Since Li is progressively concentrated in magmas evolving to silicic compositions, the low Li abundance of glass from the tuff of the White River Formation (compared to the crustal average of 20 ppm) is evidence for extensive mobilization of Li by groundwater. Preferential leaching of Li during the experiments is indicated by measurements and mass balance calculations (Tables 4, 6). Results for Li leachability support the findings of earlier studies of the relative mobility of selected elements during alteration of rhyolite with hot water (Ellis and Mahon, 1963, 1967). Lithium is also mobilized during low temperature hydration of massive obsidian (Zielinski and others, 1977) while uranium remains relatively immobile (Rosholt and others, 1971; Zielinski, 1977). The decoupling of Li and U mobility during <u>hydration</u> invalidates the use of Li as an indicator of U mobilization unless additional evidence exists for glass <u>dissolution</u>.

Future Studies

Continuing investigations of the leachability of uranium from rhyolitic glass shards will attempt to measure the relative importance of pressure, temperature, flow rate, and solution composition for determining the rate of uranium mobilization under open system conditions in which glass dissolution is occurring. Additional sampling of interstitial solutions in contact with glass shards for variable lengths of time under closed system conditions (equivalent to very slow flow rates) will attempt to monitor changes of uranium concentration after glass reaches its equilibrium solubility and in the presence of alteration products.

Conclusions

Experimental leaching of rhyolitic glass shards in an experimental apparatus designed to simulate contact of unconsolidated, air-fall ash with silica undersaturated, alkaline (pH $\approx$ 10), oxidizing groundwater has lead to the following conclusions.

1) The weight fraction of uranium released from an aliquot of glass is in good agreement with the weight fraction of silica dissolved, as long as the solution is silica undersaturated.

2) For conditions of identical temperature, pressure, leach-solution composition, and flow rate, natural rhyolite glass liberates uranium and silica more rapidly than rhyodacitic synthetic glass of comparable surface area.

3) All other conditions being equal, rhyolite glass liberates uranium and silica at rates that correlate positively with the surface area of the shards.

4) Lithium and potassium are liberated from glass at rates that are greater than observed for silica and uranium. Fluorine is liberated at rates which are equal to or less than rates for silica and uranium.

5) Based on observations of some natural rhyolite glass shards and changes produced by experimental leaching of fine-grained rhyolite glass, several tentative guides for identifying glass shards subjected to hydration and partial solution by ground water have been developed. These guides include a) surface pitting observable with the scanning electron microscope, b) thin devitrification rinds on glass surfaces observable in polished grain mounts, c) high (>50) ratios of measured surface areas compared to calculated surfaces of equivalent amounts of glass spheres of the same average diameter, and d) abnormally low (<20 ppm) Li concentrations.

Further comparison of naturally occurring rhyolite shards of different age is needed to establish the general validity of these guidelines. Generally speaking, evidence of the effects of groundwater exposure should correlate positively with the age of shards although local variations in pressure, temperature, solution composition, and flow rate may significantly effect the rates of uranium release caused by glass dissolution. The influence of these variables will be treated in a subsequent paper. Based on the preliminary evidence of this study, accumulations of secondary deposits of silica and/or lithium (lithium-rich clays) in the vicinity of ash layers can be considered evidence of hydration and partial dissolution of glassy components of ash. It is the author's experience that layers of secondary silica within air-fall ash often contain anomalous concentrations of uranium believed coprecipitated with silica from solution. A future study will investigate this process.

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Table 1

Composition of Starting Minerals

[weight percent, uncorrected for volatile constituents. Leaders denote no data]

	Glass Separate Bandelier Tuff 65 W129 (1)	Glass Separate White River Fm. (2) WTR-SB-1	Synthetic Glass GSD (3)
SiO_2	72.6	68.0	61.8
Al_2O_3	11.3	11.0	14.4
FeO	1.35+		5.29
Fe_2O_3	----	1.29++	1.54
MgO	.02	.25	3.90
CaO	.26	1.7	5.01
Na_2O	4.09	1.88	4.08
K_2O	4.56	5.5	3.72
TiO_2	.04	.17	.02
MnO	.08	.05	.04
F	.27	.08	.02
	Trace elements (ppm)		
U	14.8	5.6	40
Th	38.8	18.7	--
Li	55	6	40
Mo	----	----	46

+ all iron calculated as FeO.

++ all iron calculated as Fe_2O_3.

(1) Major element data reproduced from Izett and others, 1972.

(2) Major elements by x-ray fluorescence and atomic absorption, USGS labs.

(3) All data reproduced from Myers and others, 1976.

Table 2

Comparison of Experimental Leach Solution and Pertinent Analogs

Source	Typical concentration of major components	Typical pH	Typical ionic Strength
Groundwater draining rhyolite tuff	$\sim$.001-.005M HCO_3 [Na+K]	7-8.5	.01-.02
Groundwater draining carbonates	$\sim$.001-.01M HCO_3 [Ca+Mg+Na]	7-8.5	.01-.02
Experimental solution	.05M Na_2CO_3+.05M $NaHCO_3$	9.9	.2
Sea water	$\sim$.5M NaCl	8.15	.7
Alkaline lakes, brines	.5-5M NaCl+Na_2CO_3+$NaHCO_3$	8-10	1-10
Industrial Carbonate Leach of U ores	.25-.5M Na_2CO_3+.1-.5M $NaHCO_3$	10-11	1-2

Table 3

Analyses Schedule

<u>Solids</u> (before and after)

- Physical properties
  - Petrographic observation
  - X-ray diffraction
  - Surface area measurements - gas absorption
  - Size and shape measurements - image analyzer
  - Morphology studies - SEM
- Chemical properties
  - Electron microprobe studies of individual shards
  - Bulk chemical analyses of Si, Li, U, F
  - Uranium distribution in shards (fission track)

<u>liquids</u>

Si - colorimetric + fusion

U - fission track, fluorimetry

F - ion electrode

Li, K - atomic adsorption

Table 4: Leaching Results

		SiO_2 (ppm)	K (ppm)	Li (ppb)	F (ppm)	U (ppb)
Glass separate, Bandelier Tuff 65W129 (3.9 g)	Conc. Range	151-228	12-39	10-170	.25-.97	2.7-6.4
	Avg. Conc.* of 3810 ml	187	15.9	28	.63	3.9
	grams leached	.71	.061	$106x10^{-6}$	$2396x10^{-6}$	$14.8x10^{-6}$
	$\frac{\text{g. leached}}{\text{g. orig.}}$	.25	.43	.50	.23	.26
Glass separate, White River Fm. WTR-SB-1 (4.4 g)	Conc. Range	158-381	12-81	<10-16	.16-.50	1.7-8.1
	Avg. Conc.* of 3750 ml	256	22.9	<10	.15	2.3
	grams leached	.96	.086	$<37x10^{-6}$	$665x10^{-6}$	$8.6x10^{-6}$
	$\frac{\text{g. leached}}{\text{g. orig.}}$	.32	.44	<1.0	.19	.35
Synthetic Glass GSD (5.9 g)	Conc. Range	72-226	13-42	10-80	.08-.30	
	Avg. Conc.* of 3715 ml	191	16.4	21	∿0	14.3
	grams leached	.71	.061	$80x10^{-6}$	∿0	$53.2x10^{-6}$
	$\frac{\text{g. leached}}{\text{g. orig.}}$	.20	.34	.34	∿0	.22

Table 4 - continued

	Conc. Range	<.2	<.1-4	<10-20	.08-.20	.1-.6
Blank	Avg. Conc. of 3730 ml	<.2	<.6	<10	.12	.5
	grams leached	$<746 \times 10^{-6}$	<.002	$<37 \times 10^{-6}$	448×10^{-6}	1.9×10^{-6}

---

* corrected for blank where blank was measurable, average based on 34 100ml aliquots.

Table 5

Average Size, Degree of Roundness and Surface area of glass shards Before and After Leaching

	Mean* size φ	Std. dev. φ	$\frac{A}{p2}$**	Std. dev.	Surface area (m^2/g)	Calc.*** spherical surface areas (m^2/g)
Bandelier Tuff (Before)	3.437	.400	.046	.0009	.8±.1	.032
Bandelier Tuff (After)	3.645	.560	.048	.0007	8.5±.8	
White River Fm. (Before)	4.738	1.373	.049	.0099	3.5±.3	.064
White River Fm. (After)	4.677	1.420	.053	.0104	5.8±.6	
GSD$^{(+)}$ (Before)	5.658	.898	.061	.0094	.9±.1	.13
GSD (After)	5.399	1.010	.061	.0089	2.7±.3	

* $\phi = -\log_2$ (diam. in mm).

** area / perimeter^2. For a sphere = $1/4\pi$ = .08.

\+ size and shape parameters may have been altered due to ultrasonic cleaning required to disaggregate grains.

*** calculated surface area assuming grains are spheres of given average diameter and grain densities = 2.3g/cm^3.

Table 6

Minor element contents of glass shards before and after experimental leaching [Leaders denote no data]

Ash	Li (ppm) ± 10%	Th (ppm) ± 10%	U (ppm) ± 10%	F (wt. percent) ± 10%
Bandelier Tuff (Before)	55	38.8	14.8	.27
Bandelier Tuff (After)	45	37.9	13.8	.27
calculated*	37	----	14.4	.27
White River Fm. (Before)	6	18.7	5.6	.08
White River Fm. (After)	<5	18.7	5.3	.08
calculated*	--	----	5.35	.09
GSD (Before)	40	----	40	.02
GSD (After)	34	----	40	<.04
calculated*	33	----	38.7	.02

* calculated elemental concentration in the residuum assuming dissolution of starting material to the extent indicated by silica removal and removal of minor elements in the amounts measured in leachate solutions (Table 4).

Figure Captions

Figure 1: Schematic diagram of the experimental leaching apparatus.

Figure 2: Sample holder. Scale ≈ 1:1

Figure 3: Uranium and silica contents of the first 20 ml of Bandelier Tuff leachate #33 collected as aliquots of 2 ml.

Figure 4: Scanning electron micrographs showing surface pits in glass shards of the White River Formation, Shirley Basin, Wyoming. Scale calibration is given in microns.

Figure 5: X-ray diffraction patterns for glass shards before and after experimental treatment.

a) Bandelier Tuff (65W129)
b) Tuff of White River Formation (WTR-SBI)
c) Synthetic glass (GSD)

NOTE: Ksp = Potassium feldspar
Ca = calcite

fig 1

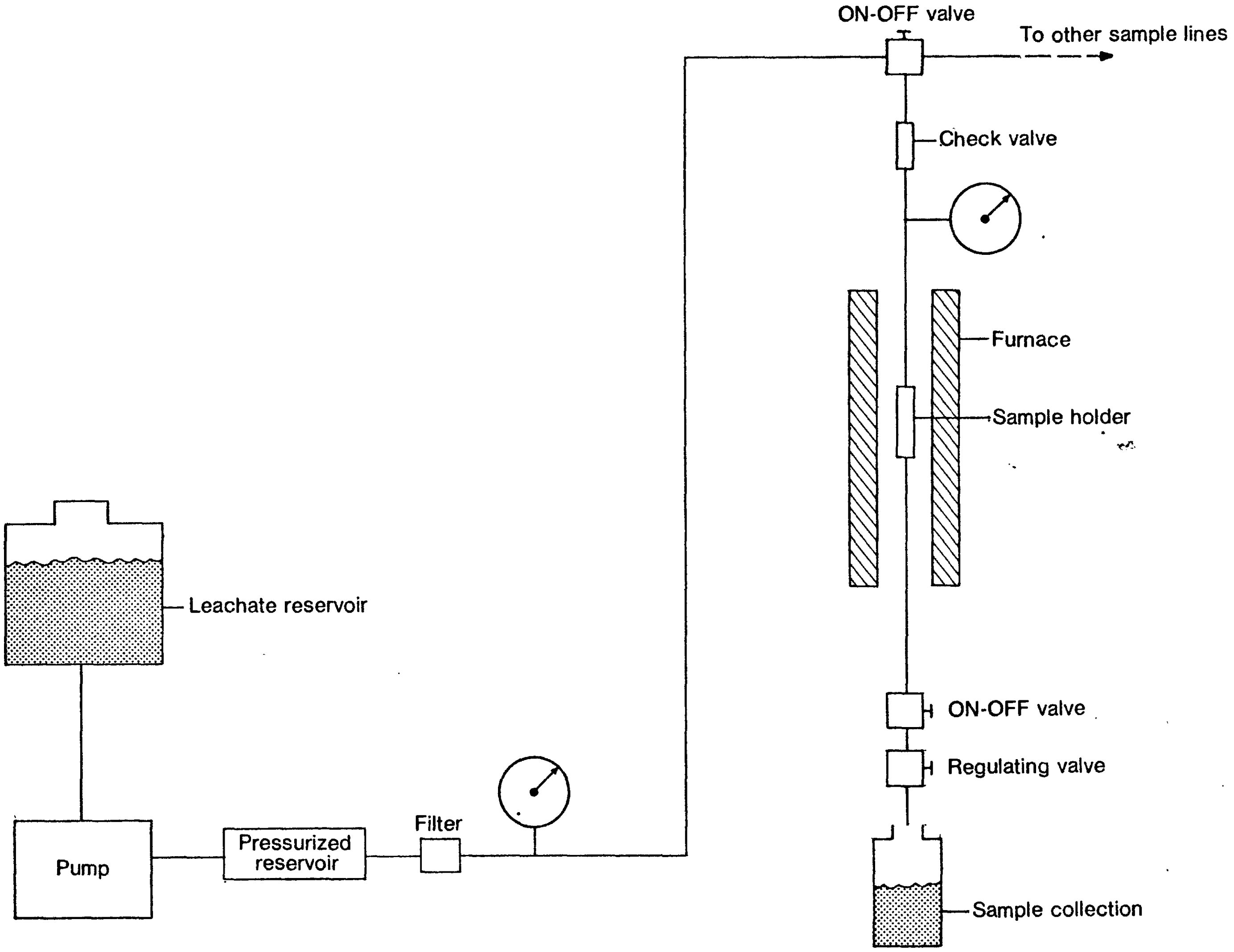

ON-OFF valve
To other sample lines
Check valve
Furnace
Sample holder
Leachate reservoir
ON-OFF valve
Regulating valve
Filter
Pressurized reservoir
Pump
Sample collection

Fig 2.

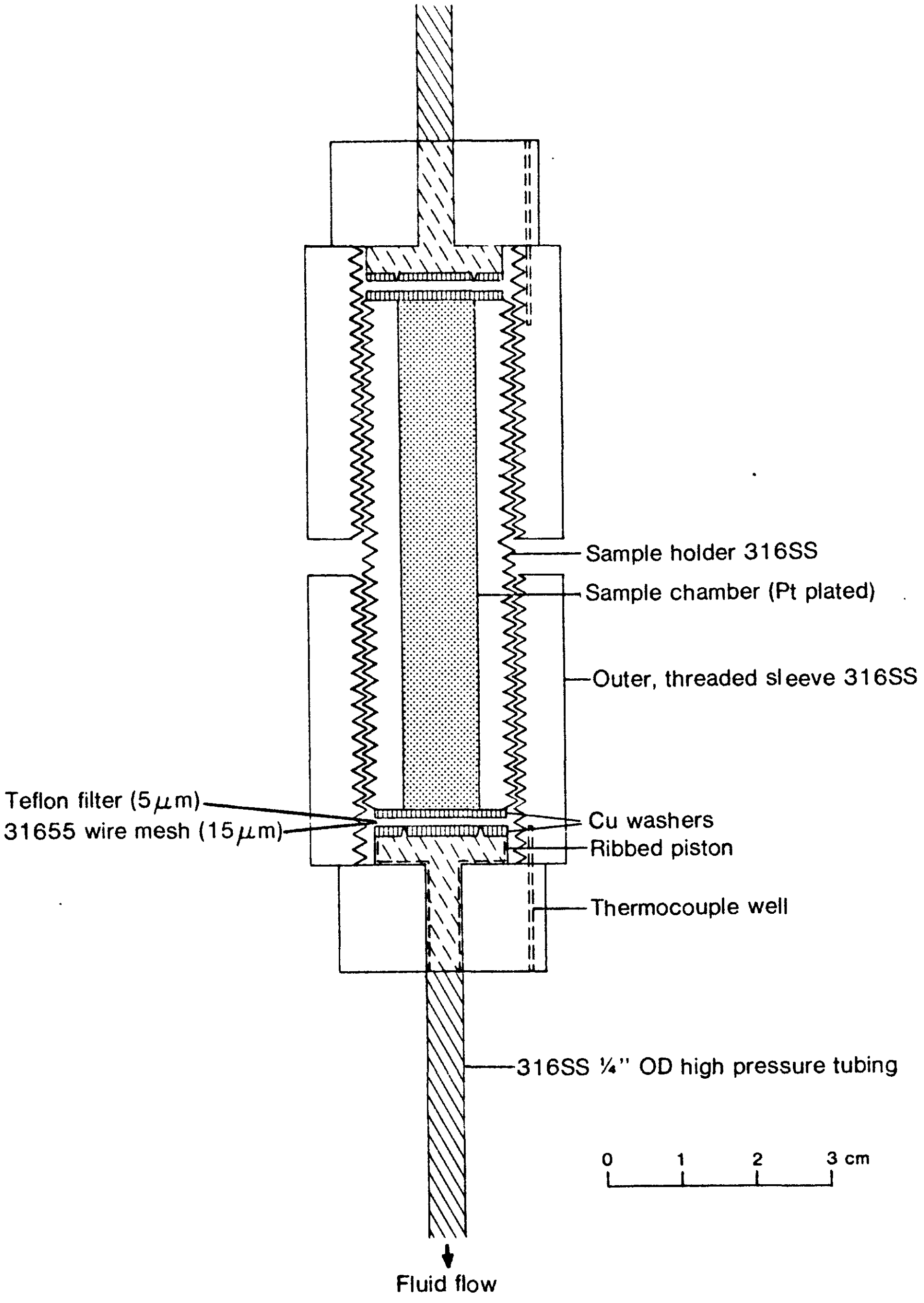
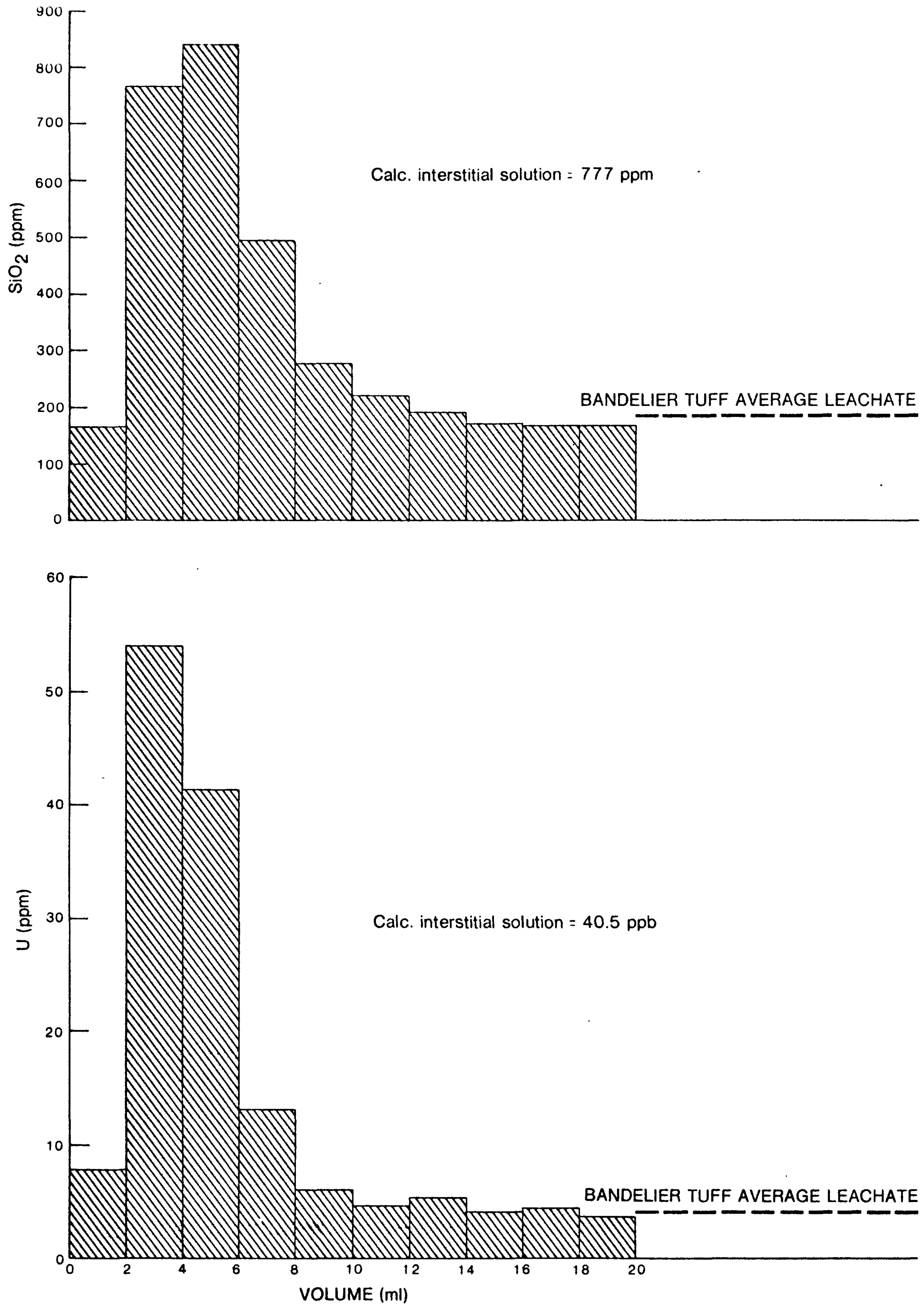
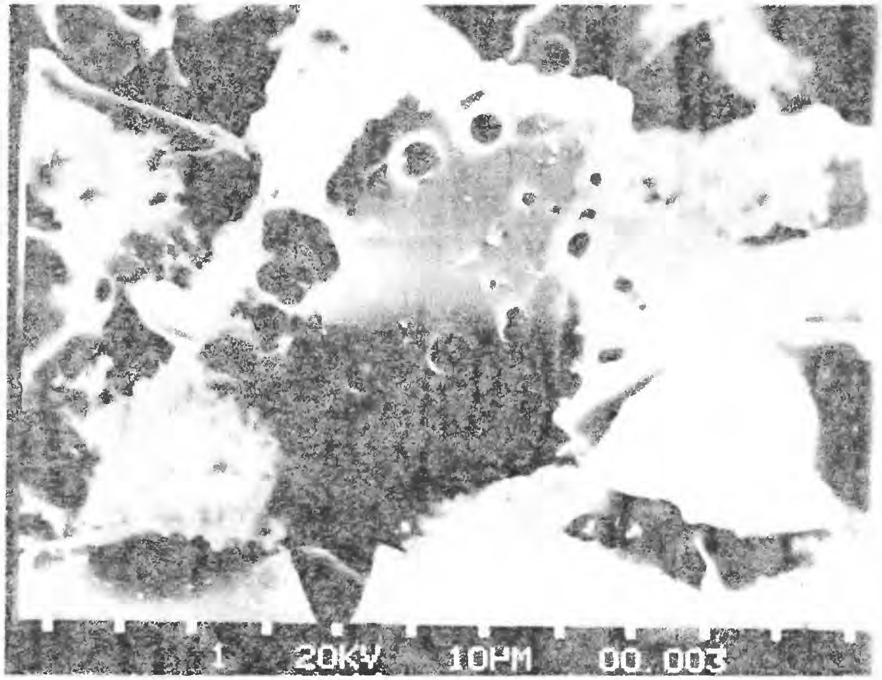
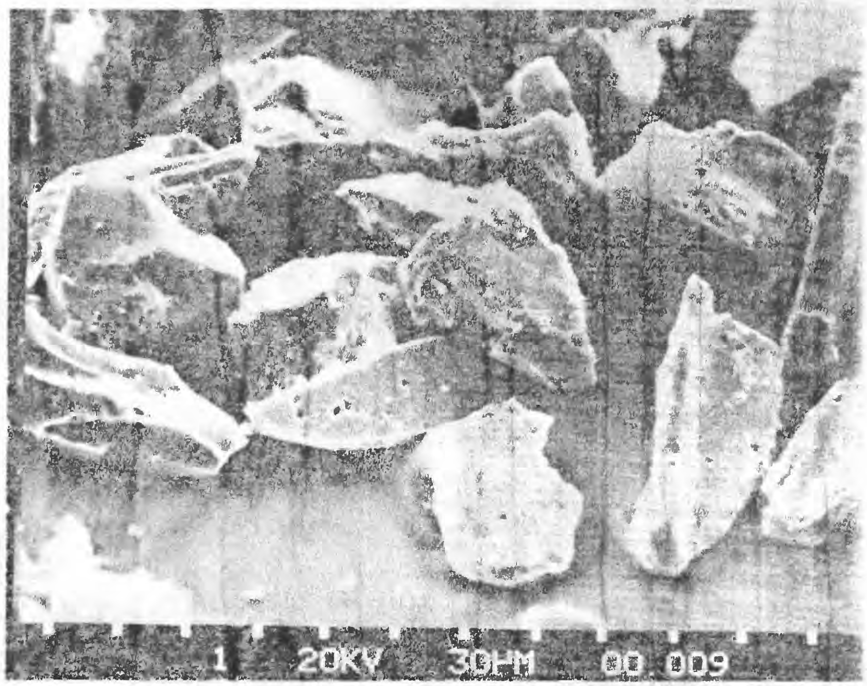

Sample holder 316SS
Sample chamber (Pt plated)
Outer, threaded sleeve 316SS
Teflon filter (5μm)
31655 wire mesh (15μm)
Cu washers
Ribbed piston
Thermocouple well
316SS ¼" OD high pressure tubing
0
1
2
3 cm
Fluid flow

fig 3

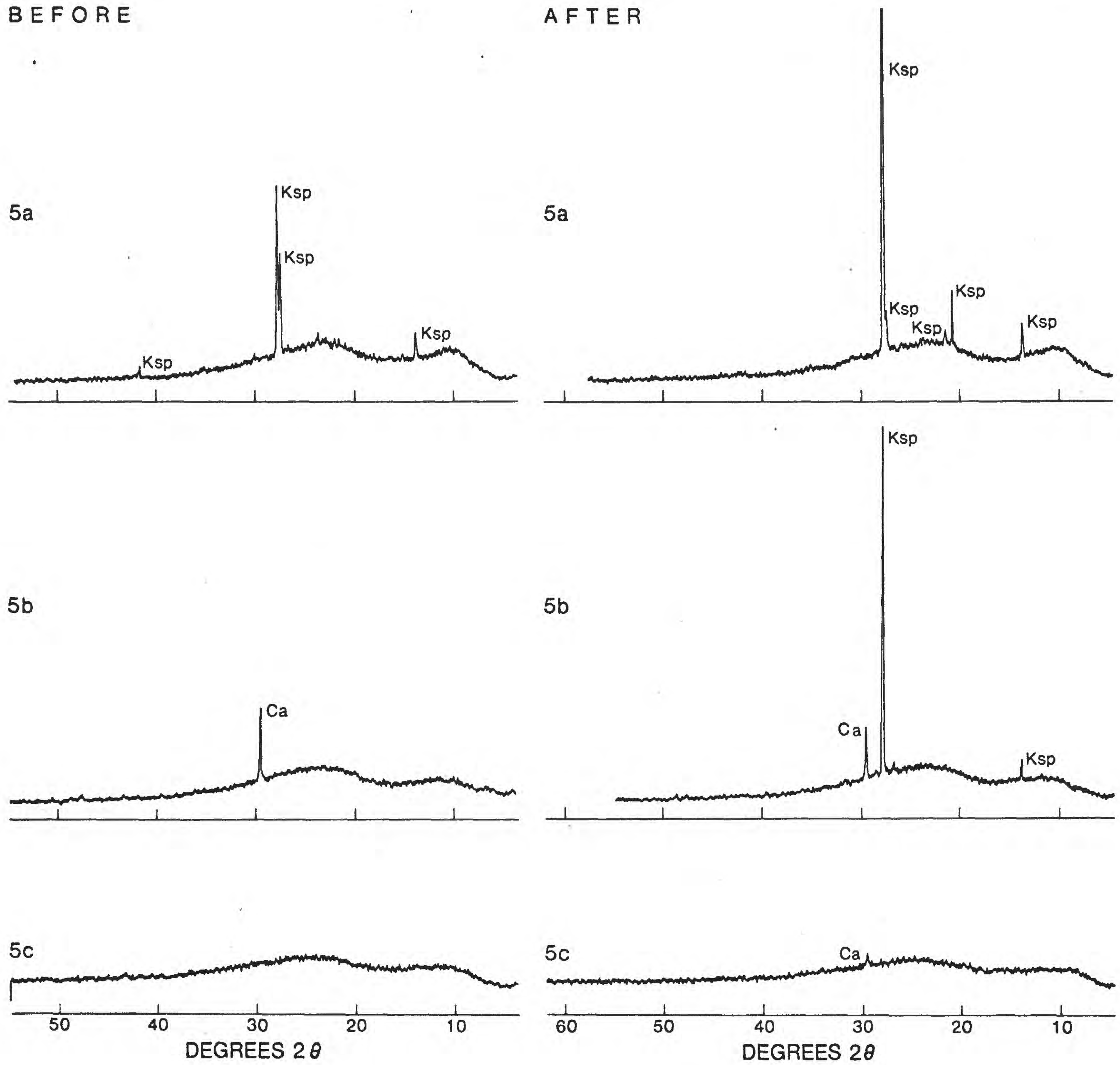

900
800
700
600
500
400
300
200
100
0
SiO_2 (ppm)
Calc. interstitial solution = 777 ppm
BANDELIER TUFF AVERAGE LEACHATE
60
50
40
30
20
10
0
U (ppm)
Calc. interstitial solution = 40.5 ppb
BANDELIER TUFF AVERAGE LEACHATE
0
2
4
6
8
10
12
14
16
18
20
VOLUME (ml)



WIR 1-41 a



WIR 1-34 C


BEFORE
AFTER
5a
Ksp
Ksp
Ksp
Ksp
5a
Ksp
Ksp
Ksp
Ksp
Ksp
5b
Ca
5b
Ksp
Ca
Ksp
5c
5c
Ca
50
40
30
20
10
DEGREES 2θ
60
50
40
30
20
10
DEGREES 2θ