Waste Isolation Safety Assessment Program

**Controlled Sample Program
Publication No. 1
Characterization of Rock
Samples**

L. L. Ames

October 1978

Prepared for the
Office of Nuclear Waste Isolation
under its Contract with the
U.S. Department of Energy

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute

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PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
Under Contract EY-76-C-06-1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151

Price: Printed Copy \$____*; Microfiche \$3.00

*Pages	NTIS Selling Price
001-025	\$4.00
026-050	\$4.50
051-075	\$5.25
076-100	\$6.00
101-125	\$6.50
126-150	\$7.25
151-175	\$8.00
176-200	\$9.00
201-225	\$9.25
226-250	\$9.50
251-275	\$10.75
276-300	\$11.00

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WASTE ISOLATION SAFETY ASSESSMENT PROGRAM

CONTROLLED SAMPLE PROGRAM
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CHARACTERIZATION OF ROCK SAMPLES

L. L. Ames

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Prepared for the
Office of Nuclear Waste Isolation
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Pacific Northwest Laboratory
Richland, Washington 99352

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SUMMARY

The primary objective of this report is to describe the methodology used and the geologic parameters measured on several rocks which are being used in "round-robin" laboratory and nuclide adsorption methodology experiments. Presently investigators from various laboratories are determining nuclide distribution coefficients utilizing numerous experimental techniques. Unfortunately, it appears that often the resultant data are dependent not only on the type of groundwater and rock utilized, but also on the experimenter or method used. The Controlled Sample Program is a WISAP (Waste Isolation Safety Assessment Program) attempt to resolve the apparent method dependencies and to identify individual experimenter's bias.

The rock samples characterized in an interlaboratory Kd methodology comparison program include Westerly granite, Argillaceous shale, Oolitic limestone, Sentinel Gap basalt, Conasauga shale, Climax Stock "granite", anhydrite, Magenta dolomite and Culebra dolomite. Techniques used in the characterization include whole rock chemical analysis, X-ray diffraction, optical examination, electron microprobe elemental mapping and chemical analysis of specific mineral phases. Surface areas were determined by the B.E.T. and ethylene glycol sorption methods. Cation exchange capacities were determined with ^{85}Sr , but were of questionable value for the high calcium rocks. A quantitative mineralogy was also estimated for each rock.

Characteristics which have the potential of strongly affecting radionuclide Kd values such as the presence of sulfides, water-soluble, pH-buffering carbonates, glass, and ferrous iron were listed for each rock sample.

CONTENTS

SUMMARY	iii
LIST OF FIGURES	vi
LIST OF TABLES	ix
ACKNOWLEDGMENTS	xi
INTRODUCTION	1
CHARACTERIZATION METHODS	5
RESULTS	15
WHOLE-ROCK CHEMICAL ANALYSIS	15
X-RAY DIFFRACTION	15
OPTICAL EXAMINATION	17
Westerly Granite	17
Argillaceous Shale	20
Oolitic Limestone	20
Sentinel Gap Basalt	20
Conasauga Shale	27
Climax Stock Granite	27
Anhydrite	27
Magenta Dolomite	27
Culebra Dolomite	33
ELECTRON MICROPROBE ELEMENTAL MAPPING	33
Westerly Granite	33
Argillaceous Shale	43
Oolitic Limestone	43
Sentinel Gap Basalt	43
Conasauga Shale	59
Climax Stock Granite	59
Anhydrite	59
Magenta Dolomite	72
Culebra Dolomite	72
ELECTRON MICROPROBE CHEMICAL ANALYSIS	81
Westerly Granite	81

CONTENTS (contd)

Argillaceous Shale	83
Oolitic Limestone	83
Sentinel Gap Basalt	83
Conasauga Shale	87
Climax Stock Granite	87
Anhydrite	87
Magenta Dolomite	90
Culebra Dolomite	91
B.E.T. SURFACE AREA	92
ETHYLENE GLYCOL SORPTION SURFACE AREA	93
STRONTIUM CATION EXCHANGE CAPACITY	94
ESTIMATION OF QUANTITATIVE MINERALOGY	95
PERTINENCE OF CHARACTERIZATION DATA TO K _d DETERMINATIONS	97
REFERENCES	100
DISTRIBUTION LIST	Distr-1

LIST OF FIGURES

1. Sentinel Gap Basalt Feldspar Composition	10
2. Sentinel Gap Basalt Pyroxene Composition	11
3. Sentinel Gap Basalt Fragment	13
4. Westerly Granite	18
5. Westerly Granite	19
6. Argillaceous Shale	21
7. Argillaceous Shale	22
8. Oolitic Limestone	23
9. Oolitic Limestone	24
10. Sentinel Gap Basalt	25
11. Sentinel Gap Basalt	26
12. Conasauga Shale	28
13. Conasauga Shale	29
14. Climax Granite	30
15. Climax Granite	31
16. Anhydrite	32
17. Magenta Dolomite	34
18. Magenta Dolomite	35
19. Culebra Dolomite	36
20. Westerly Granite	37
21. Westerly Granite	38
22. Westerly Granite	39

LIST OF FIGURES (contd)

23.	Westerly Granite	40
24.	Westerly Granite	41
25.	Westerly Granite	42
26.	Argillaceous Shale	44
27.	Argillaceous Shale	45
28.	Argillaceous Shale	46
29.	Argillaceous Shale	47
30.	Argillaceous Shale	48
31.	Argillaceous Shale	49
32.	Oolitic Limestone	50
33.	Oolitic Limestone	51
34.	Oolitic Limestone	52
35.	Oolitic Limestone	53
36.	Oolitic Limestone	54
37.	Sentinel Gap Basalt	55
38.	Sentinel Gap Basalt	56
39.	Sentinel Gap Basalt	57
40.	Sentinel Gap Basalt	58
41.	Conasauga Shale	60
42.	Conasauga Shale	61
43.	Conasauga Shale	62
44.	Conasauga Shale	63

LIST OF FIGURES (contd)

45.	Climax Granite	64
46.	Climax Granite	65
47.	Climax Granite	66
48.	Climax Granite	67
49.	Anhydrite	68
50.	Anhydrite	69
51.	Anhydrite	70
52.	Anhydrite	71
53.	Magenta Dolomite	73
54.	Magenta Dolomite	74
55.	Magenta Dolomite	75
56.	Magenta Dolomite	76
57.	Culebra Dolomite	77
58.	Culebra Dolomite	78
59.	Culebra Dolomite	79
60.	Culebra Dolomite	80

LIST OF TABLES

1. Rocks Utilized in the 20 to 40 Mesh Size Range in Task 4 Studies	2
2. Techniques Used to Characterize the 20 to 50 Mesh Rock Samples	6
3. Precision of X-ray Fluorescence Analyses at 95% Confidence Limits	6
4. Sentinel Gap Basalt Feldspar Computations	9
5. Whole Rock Chemical Analyses of the 20 to 50 Mesh Standard Samples	16
6. The Major Mineral Phases Found in X-ray Diffraction Tracings of As-Received, Standard Rock Samples	17
7. Microprobe Chemical Analyses and Computed Compositions of Minerals in the 20 to 50 Mesh Westerly Granite	82
8. Microprobe Chemical Analyses and Computed Compositions of Minerals in the 20 to 50 Mesh Argillaceous Shale	84
9. Microprobe Chemical Analyses and Computed Compositions of Minerals in the 20 to 50 Mesh Oolitic Limestone	85
10. Microprobe Chemical Analyses and Computed Compositions of Minerals in the 20 to 50 Mesh Sentinel Gap Basalt	86
11. Microprobe Chemical Analyses and Computed Compositions of Minerals in the 20 to 50 Mesh Conasauga Shale	88
12. Electron Microprobe Chemical Analyses and Computed Compositions of Minerals in the 20 to 50 Mesh Climax Stock Granite	89
13. Microprobe Chemical Analyses and Computed Compositions of Minerals in the 20 to 50 Mesh Anhydrite	90
14. Microprobe Chemical Analyses and Computed Compositions of Minerals in the 20 to 50 Mesh Magenta Dolomite	91
15. Microprobe Chemical Analyses and Computed Compositions of Minerals in the 20 to 50 Mesh Culebra Dolomite	92

LIST OF TABLES (contd)

16.	B.E.T. Surface Areas of the 20 to 50 Mesh Standard Rock Samples	93
17.	Ethylene Glycol Sorption Surface Areas of the 20 to 50 Mesh Standard Rock Samples	94
18.	Cation Exchange Capacities of the Standard 20 to 50 Mesh Rock Samples Measured with Strontium	94
19.	Quantitative Estimation of Minerals in the 20 to 50 Mesh Standard Rock Samples	96
20.	Summary of Rock Characteristics that Could Affect Radionuclide Kd Results at Room Temperature	98

ACKNOWLEDGMENTS

This research was supported in part by the Waste Isolation Safety Assessment Program being conducted by Pacific Northwest Laboratory. This program is sponsored by the Office of Nuclear Waste Isolation, which is managed by Battelle Memorial Institute under its contract with the Department of Energy.

The author would like to acknowledge the outstanding petrographic work and optical photography of Mr. R. E. Beauchamp. The electron microprobe work, which included an estimate of several whole rock chemical analyses, was performed by Mr. Harvey Tenny. Mr. Victor Swan was responsible for the determination of the whole rock chemical analysis of the igneous rocks and argillaceous shale. The surface area analyses by ethylene glycol adsorption were performed by Mr. Dean A. Moore. The cation exchange capacities were determined by Mrs. Ann C. Campbell.

CONTROLLED SAMPLE PROGRAM
PUBLICATION NO. 1
CHARACTERIZATION OF ROCK SAMPLES

INTRODUCTION

This document is the first of several to describe the results of an experimental methodology and interlaboratory comparison program on the determination of radionuclide distribution coefficients, K_d s, for various rock and ground water combinations.

Large quantities of rocks were obtained to provide all WISAP (Waste Isolation Safety Assessment Program, one effort of the National Waste Terminal Storage Program being managed by the Office of Nuclear Waste Isolation) Task 4 subcontractors with selected common samples. Through the use of common samples it should be possible to compare K_d data between the various labs and between different experimental techniques. The main objectives are: 1) to ascertain whether different experimenters obtain the "same" results using common rocks, standard solutions and a dictated experimental design and 2) to ascertain the comparability of results obtained by individual laboratories using different experimental methodologies. The latter study will investigate K_d dependencies on experimental methodologies in hopes of formulating a standard " K_d " method, or to derive calibration numbers to convert K_d numbers derived from one method to K_d values applicable to another method.

Samples of rocks were obtained from Department of Energy contractors and from Wards Natural Science Establishment, Inc. Details on the as-received rocks are listed in Table 1. Through the use of a jaw crusher and grinder, these rocks were reduced in size. A 20 to 50 mesh size fraction (0.85 to 0.30 mm) was recovered from the ground material by screening. The relatively large size fraction was selected for several reasons: (a) to reduce any effects on sorption caused by grinding, (b) to attempt to reduce iron contamination due to fragmenting off the

TABLE 1. Rocks Utilized in the 20 to 50 Mesh Size
Range in Task 4 Studies

Rock	Source	Donor
Westerly Granite	New England	Lawrence Livermore Labs Hugh Heard
Argillaceous Shale (Green)	New York State	Wards Natural Science Establish. Cat. No. 47W7400
Oolitic Limestone	Indiana	Wards Natural Science Establish. Cat. No. 47W4670
Sentinel Gap Basalt	Washington State Hiway 243 Road outcrop between Beverly and Mattawa, WA	Pacific Northwest Laboratory, L. L. Ames
Conasauga Shale	Core Well No. OWI-OR-8 depth 16 to 100 ft	Oak Ridge National Lab L. R. Dole
Climax Stock "Granite"	Pile driver tunnel complex, 1367 ft below the collar of shaft 1501 Nevada State N901, 147 E 677,016	Lawrence Livermore Labs L. D. Ramspott
Anhydrite	Core Well AEC 8 depth 3080.9 - 3083.5 ft Los Medanos, N. Mexico	Sandia Laboratories D. W. Powers
Magenta Dolomite Rustler Formation	Roadcut along N. M. Hiway 31 near entrance to IMC mine Sec 1, T22S, R29E	Sandia Laboratories D. W. Powers
Culebra Dolomite Rustler Formation	Roadcut along N. M. Hiway 62/180 about 7 miles South of Carlsbad airport, SEC 4 T24S, R26E	Sandia Laboratories D. W. Powers

crusher, and (c) to avoid crushing the materials to a small size fraction below a practical limit for running flow-through column experiments. Subsequently an investigator determined that iron contamination was present in the basalt and possibly westerly granite samples. The alternative would have been to reduce the rocks in size in alumina or agate apparatus, a very time consuming, tedious and expensive undertaking. The primary objective was to produce samples that could be used in comparative radionuclide Kd determinations, not necessarily to produce absolutely contamination-free samples.

CHARACTERIZATION METHODS

The techniques used to characterize each rock sample are listed in Table 2. The whole-rock chemical analyses were performed at Washington State University on the 20 to 50 mesh samples. Approximately 20 grams of a quartered sample was placed in a swingmill where it was ground for six minutes. This provided a fine, even-grained powder that was essential to the production of homogeneous samples. Seven grams of lithium tetraborate and 3.5 grams of the rock powder were thoroughly mixed and fused in a graphite crucible at 1000 C for five minutes. Upon cooling, the lithium tetraborate bead was removed from the crucible, and the basal surface of the bead ground flat. The flat bead surface was irradiated in a Philips P.W. 1410 manual spectrometer with a chromium tube. The count rate recorded for each major element was related to the calibration curves derived from the count rates of similar analyzed samples supplied by the U.S. Geologic Survey and the National Bureau of Standards. A computer program was used to make spectral corrections, and to determine the elemental oxide values. The precision for each major element is given in Table 3 calculated from $\pm$ two standard deviations, , of triplicate analyses.

Certain of the chemical constituents including carbon dioxide, sulfur and plus 105 C water, were not determinable by X-ray fluorescence analysis. Carbon dioxide was determined by measurement of the volume of gas formed during an acid digestion of a weighed quantity of powdered rock. Sulfate was determined by a gravimetric method. A weighed sample of powdered rock was fused with sodium carbonate, dissolved in HCl and recovered and weighed as BaSO_4 by addition of BaCl_2 solution. Sulfur was reported as SO_3 , and was only determined when the X-ray diffraction tracings showed that gypsum or anhydrite was present in the rock. In addition, water lost between 105 C and 250 C was determined on weighed rock samples known to contain gypsum or anhydrite from their X-ray tracings.

TABLE 2. Techniques Used to Characterize the
20 to 50 Mesh Rock Samples

1. Whole-Rock Chemical Analysis
2. X-ray Diffraction
3. Optical Examination
4. Electron Microprobe Elemental Mapping
5. Electron Microprobe Chemical Analysis
6. B.E.T. Surface Area
7. Ethylene Glycol Sorption Surface Area
8. Strontium Cation Exchange Capacity
9. Estimation of Quantitative Mineralogy

TABLE 3. Precision of X-ray Fluorescence Analyses at 95%
Confidence Limits. Thirteen sets of triplicate
beads were used.

<u>Major Elements</u>	<u>Total Analytical Precision, 2σ (in %)</u>
SiO ₂	0.550
Al ₂ O ₃	0.310
TiO ₂	0.050
FeO	0.350
MnO	0.010
CaO	0.220
MgO	0.150
K ₂ O	0.030
Na ₂ O	0.160
P ₂ O ₅	0.014

X-ray diffraction was used to determine the major mineral phases present in each rock sample. It is doubtful that the phases constituting less than 10 wt% of the rock could be determined by the usual X-ray examination method. The standard technique includes crushing and grinding a representative rock sample in an alumina mortar. The minus 200 mesh whole-rock powder was placed in a tray and a Norelco X-ray diffraction unit used to obtain an X-ray diffraction tracing. Diffraction peak heights and spacings were matched to those given in the powder diffraction data for minerals published by the Joint Committee on Powder Diffraction Standards, Swarthmore, PA. Only mineral group names were identified. The feldspars and pyroxenes, for example, were not further classified because the variety of feldspar and pyroxene is more easily determined by other techniques.

Optical examinations and photography were performed on polished mounts of the 20 to 50 mesh rock samples. A few grams of a representative 20 to 50 mesh rock sample was mixed with a thermal-setting epoxy resin, solidified at 80°C and the face of the mount containing the sample fragments ground and polished. Photographs of several areas of the mount as viewed in a Zeiss Ultraphot IIIB petrographic microscope were obtained at several magnifications.

The electron microprobe can be used to map the surface elements in an area of the polished mount. The mounts were first gold-coated in a vacuum to insure electrical conductivity on the polished surface. A selected area on the mount, usually at a magnification of 100X, was scanned and the counts from characteristic elemental X-ray emissions were stored. A photograph of selected X-ray emissions characteristic of each major constituent element was taken from the oscilloscope tracings. While the quantity of each element is directly proportional to the amount present in the scanned surface, the results are only qualitative due to a lack of matrix absorption corrections necessary for quantitative results. A computer program that included several corrections compared similar standard counts with unknown elemental X-ray emission counts to produce a quantitative metal oxide result that was within plus or minus five percent

of the actual constituent values. The lower detection limit on the microprobe was usually 0.1 wt% of the elemental oxide. Sodium, the lightest element that could be quantitatively determined on the microprobe, was an exception with 1.3 wt% of the lower sodium detection limit.

An example of the method used to compute a feldspar molecule containing 32 oxygen atoms is shown in Table 4. The as-received microprobe analysis was divided by a molecular weight that includes a single cation only, to yield the cation proportions in the analysis. The cations were recomputed to 100% and the oxygen atoms associated with each cation were summed. From the oxygen sum, the factor required to relate the total number of oxygen atoms to 32 was computed, and this factor used to determine the cations associated with 32 oxygen atoms. Ideally, the computations should result in a 32 oxygen feldspar molecule of $(\text{Na, Ca, K})_{4.00} (\text{Al, Si})_{16.00} \text{O}_{32}$. However, the analysis was considered acceptable if the determined subscripts were within plus or minus five percent of the ideal subscripts (4.00 and 16.00).

In addition, the atom percentages of potassium, sodium and calcium feldspar molecules were determined and the resulting percentages located on the feldspar compositional diagram shown in Figure 1. From the resulting compositional point, the variety of plagioclase, for example, can be ascertained. Pyroxenes refer to a molecule containing six oxygen atoms and can be identified on a FeSiO_3 - CaSiO_3 - MgSiO_3 compositional triangle as shown in Figure 2. The determination of feldspar and pyroxene varieties often are useful in classification of the rock type. The Climax Stock "granite," for example, contained considerable andesine feldspar. Thus the rock type was granodiorite rather than granite.

The technique of Brunauer, Emmett and Teller (1938), a nitrogen or argon gas adsorption method, was used to determine specific surface areas of the 20 to 50 mesh rock samples. Another method used was that of ethylene glycol adsorption first proposed by Hendricks and Dyal (1950) and further refined by Rai and Franklin (1978). Supposedly the B.E.T. method measures only external surface areas, while glycol adsorption measures

TABLE 4. Sentinel Gap Basalt Feldspar Computations

	<u>wt%</u>	<u>Equivalent Molecular Weight</u>	<u>Cation Proportions</u>	<u>100%</u>	<u>Associated Oxygen</u>	<u>Cations Related to 32 Oxygen Atoms</u>
SiO ₂	60.5	60.06	1.007	54.20	108.40	10.74
Al ₂ O ₃	24.4	50.98	0.479	25.78	38.67	5.11
CaO	9.3	56.08	0.166	8.93	8.93	1.77
K ₂ O	0.9	47.10	0.019	1.02	0.51	0.20
Na ₂ O	5.8	31.00	<u>0.187</u>	10.06	<u>5.03</u>	1.99
			$\frac{100}{1.858} = 53.821$	$\frac{161.54}{32} = 5.048$

both external and internal surfaces, with the swelling surfaces of smectite an example of the latter. In any case, the two methods do not measure the same quantities (Haynes, 1961).

The cation exchange capacities of the various 20 to 50 mesh standard samples were measured with ⁸⁵Sr tracer in a strontium chloride solution of known concentration (Routson et al., 1973). A small, two gram quantity of 20 to 50 mesh representative rock sample was placed in a 1-cm diameter tube with a fine glass frit base, and saturated with an excess of the 1N Sr solution. An equal volume of 0.05N Sr solution traced with ⁸⁵Sr was then equilibrated with the geologic material. The excess strontium solution remaining in the two gram rock sample was displaced with two alcohol washes before counting.

The comparison of counts on the rock sample to counts in a similar volume of solution of known concentration allowed computation of the amount of strontium retained by exchange on the two gram rock sample. The cation exchange capacity is not an absolute value but varies to a greater or lesser extent as a function of the cation, pH and procedure used in the capacity determination.

FIGURE 1.

FIGURE 2.

Certain of the polished mount photographs showed enough color contrast to allow their use with a film density scanning system called a Quantimet which effectively differentiates, counts and sums a series of picture points, yielding a quantitative estimate of rock mineralogy. The process is similar to that of petrographic point counting, but much less tedious, more rapid and probably more accurate. A photograph of a Sentinel Gap basalt fragment used in the quantitative mineralogical work is shown in Figure 3. The Quantimet differentiates a white phase (metallics), a light gray phase (pyroxenes), a dark gray phase (plagioclases), a black phase (clays, mineraloids) and the interstitial groundmass area by difference between the total area minus the sum of the above phase areas. Unfortunately the contrast between phases is not always great enough to allow the use of the Quantimet. Other methods such as classical point counting often must be used for an estimate of quantitative rock mineralogy.

FIGURE 3.

RESULTS

WHOLE ROCK CHEMICAL ANALYSIS

The whole rock chemical analyses of the 20 to 50 mesh rock samples are listed in Table 5. The CO_2 , SO_3 and H_2O values were obtained by standard wet chemical analytical methods other than X-ray fluorescence analysis. The computer program associated with the analytical method produces an analysis that always sums to 100 wt%. However, the proportions between cation analytical values remain the same. As can be seen from the duplicate analyses of two quartered portions of the argillaceous shale and Sentinel Gap basalt, the 20 to 50 mesh material was well-mixed. The iron in the standard rock samples was determined as elemental iron and reported as ferrous iron (Fe^{2+}). The actual ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$ in the samples is unknown.

In addition to the major rock constituents reported in Table 5, there are often one or more minor constituents that are of interest to experimentalists performing radionuclide distribution coefficient measurements. These were investigated and will be reported in a later section.

The Westerly granite, which makes up the U.S. Geological Survey standard granite samples G-1 and G-2, is one of the most intensively studied rock standards (Chayes, 1951; Stevens and Niles, 1960; Friedman, 1960; Fleischer and Stevens, 1962; Flanagan, 1967). The G-2 sample location was approximately three miles from G-1, and the Westerly granite from G-2 location contained less quartz and microcline than G-1 location granite (69.2 wt% SiO_2 at G-2 compared to 72.2 wt% SiO_2 at G-1). The Westerly granite sample analysis in Table 5 is nearly identical to that given for G-2 by Flanagan (1967).

X-RAY DIFFRACTION

Representative samples of the 20 to 50 mesh rock samples were ground and X-ray diffraction patterns obtained on the as-received powders. The results are given in Table 6. No attempt to identify the varieties of

TABLE 5. Whole Rock Chemical Analyses of the 20 to 50 Mesh Standard Samples

Constituent	Westerly Granite	Argillaceous Shale		Oolitic Limestone	Sentinel Gap Basalt		Conasauga Shale	Climax Stock Granite	Anhydrite	Magenta Dolomite	Culebra Dolomite
SiO ₂	69.76	61.31	61.68	0.25	53.96	54.02	65.58	68.41	0.01	6.28	1.10
Al ₂ O ₃	16.69	20.59	20.42	0.10	13.89	13.89	19.10	16.38	0.01	1.41	0.50
TiO ₂	0.38	1.03	1.03	0.01	1.94	1.95	0.78	0.37	BDL	0.04	0.02
FeO	2.17	5.31	5.28	0.11	12.27	12.29	7.42	2.45	0.01	0.29	0.27
MnO	0.04	0.04	0.04	BDL	0.20	0.20	0.11	0.06	0.01	BDL	0.04
CaO	2.01	1.58	1.55	55.73	8.46	8.39	0.89	3.72	23.76	31.00	29.73
MgO	1.12	3.14	3.15	BDL	4.33	4.37	1.75	1.05	7.94	10.69	21.03
K ₂ O	4.48	6.44	6.37	0.02	1.20	1.19	3.68	3.91	BDL	0.29	0.28
Na ₂ O	3.27	0.40	0.32	BDL	3.43	3.39	0.56	3.55	3.75	0.91	0.02
P ₂ O ₅	0.08	0.16	0.16	0.05	0.32	0.31	0.13	0.10	0.03	0.03	0.15
SO ₃	NA	NA	NA	NA	NA	NA	NA	NA	54.28	26.14	NA
CO ₂	NA	NA	NA	43.73	NA	NA	NA	NA	8.67	11.15	46.59
H ₂ O	NA	NA	NA	NA	NA	NA	NA	NA	1.53	11.76	NA
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

NA = not analyzed

BDL = below detection limits, usually 0.1 wt%

TABLE 6. The Major Mineral Phases Found in X-Ray Diffraction Tracings of As-Received, Standard Rock Samples

<u>Rock</u>	<u>Major Mineral Phases</u>
Westerly Granite	Feldspar, quartz, mica
Argillaceous Shale	Quartz, illite, kaolinite
Oolitic Limestone	Calcite
Sentinel Gap Basalt	Feldspar, pyroxene
Conasauga Shale	Quartz, kaolinite, illite, feldspar
Climax Stock	Feldspar, quartz, mica
Anhydrite	Anhydrite, magnesite
Magenta Dolomite	Gypsum, calcite, dolomite
Culebra Dolomite	Dolomite

feldspar, mica, or pyroxene was made at this time because later microprobe chemical analyses yielded data on exact varietal identifications.

The major mineral phases of Table 6 are listed in their estimated order of occurrence from greater to lesser amounts. Gypsum and calcite appeared as the major mineral phases in Magenta dolomite. Thus Magenta gypsum would be a somewhat more descriptive rock name than dolomite.

OPTICAL EXAMINATION

In almost all instances during characterization work (optical microscopy and microprobe) three randomly chosen areas were analyzed for each sample. The enclosed figures designate these three areas as A, B, and C. There is no significance to these designations other than their use for bookkeeping. Magnifications are given in the lower right hand corner for each area shown. The following abbreviations are used: D.F. is dark field and B.F. is bright field.

Westerly Granite

Optical views of the 20 to 50 mesh westerly granite, mounted in epoxy, ground and polished, are shown in Figures 4 and 5. The three

50X

D.F.

12X

B.F.

12X

WESTERLY GRANITE

FIGURE 4.

A

200X

B

200X

C

200X

WESTERLY GRANITE

FIGURE 5.

areas of Figure 5 that were magnified 200 times (selected areas A, B, and C) also are shown in the next section as elemental maps, though not always from the same viewpoint. As can be seen from Figure 4, the contrast between quartz and the feldspars by reflected light is poor. Consequently, the use of a film density measuring device to determine quantitative mineralogy was not feasible. Other methods based on petrographic examination were required. The various mineral phases shown in the optical photographs were identified during elemental mapping and microprobe chemical analyses.

Argillaceous Shale

The shale is composed of relatively coarse to very fine grained materials as seen in Figures 6 and 7. As indicated by the X-ray diffraction work, the finer matrix materials are probably the illite and kaolinite, and the coarser materials probably quartz and calcite.

Oolitic Limestone

Optical views of the limestone shown in Figures 8 and 9 show many unusual physical features but X-ray diffraction results indicated that only calcite was present as a major mineral phase. The scratches in the upper and lower edges of the 12X B.F. area were used by the microprobe operator to relocate specific areas for microprobe examination.

Sentinel Gap Basalt

The four major basalt mineral phases can be readily seen in the optical photographs in Figures 10 and 11 of the 20 to 50 mesh Sentinel Gap basalt. The gray material between the basalt fragments is the epoxy plastic. An excellent polish was attained on these mounts as evidenced by the fact that very few scratches can be seen in the mounting plastic even at the 100X magnification in Figure 11. The lightest color in the reflected light photographs of Figure 11 is due to metallic oxides such as magnetite or ilmenite. The light gray areas are reflected from pyroxenes, the darker gray reflections are due to plagioclase crystals and the black areas represent clay minerals and uncrystallized iron and silicon hydrated oxides (mineraloids).

ARGILLACEOUS SHALE

FIGURE 6.

A

100X

B

100X

C

100X

ARGILLACEOUS SHALE

FIGURE 7.

OOLITIC LIMESTONE

FIGURE 8

A

100X

B

100X

C

100X

OOBITIC LIMESTONE

FIGURE 9.

50X

D.F.

12X

B.F.

12X

SENTINEL GAP

FIGURE 10.

A

100X

B

100X

SENTINEL GAP

FIGURE 11.

Conasauga Shale

Coarser-grained fragments of quartz and feldspars can be seen embedded in a kaolinite-illite matrix in Figures 12 and 13. This shale contains more coarse detrital material than does the argillaceous shale. Enlarged (100X) areas were from the 50X area as indicated by the A, B and C notation.

Climax Stock Granite

Optical views of the Climax Stock 20 to 50 mesh rock sample are shown in Figures 14 and 15. Contaminating iron from the crushing and grinding equipment were specifically sought in the eight times magnifications, with confirmation by microprobe chemical analysis. A few iron pieces were found in the harder rocks such as the basalt, but they are relatively scarce. The metallic-like fragment shown in area B of Figure 15, for example, was a calcium titanate (sphene) normally found in granitic type rocks, and not a machinery fragment that would be nearly pure iron. Area A of Figure 14 shows a biotite mica crystal containing small amounts of numerous other minerals.

Anhydrite

Optical photographs of the anhydrite are given in Figure 16. The X-ray diffraction tracings and whole-rock analysis indicated magnesite admixed with the anhydrite. The anhydrite is the major mineral phase and is probably present as the larger, light gray crystals, while the magnesite is present as areas of smaller crystals embedded in the anhydrite. It is not unusual to find that a chemical precipitate such as anhydrite is admixed with other mineral phases. Anhydrite hydrates to gypsum at room temperature, although the process is very slow.

Magenta Dolomite

The Magenta was referred to as a dolomite, which it may well be elsewhere in the geologic strata. However, at the sample locality of this rock, the major mineral phase is gypsum. The relatively small amount of MgO indicated in the whole rock analysis for the Magenta was another indication that other calcium compounds were present besides dolomite.

50X

8X

A

100X

CONASAUGA

FIGURE 12.

B

100X

C

100X

CONASAUGA

FIGURE 13.

50X

8X

A

200X

CLIMAX GRANITE

FIGURE 14.

B 200X

C 200X

CLIMAX GRANITE

FIGURE 15

50X

8X

A

200X

B

200X

ANHYDRITE

FIGURE 16.

The optical photographs are shown in Figure 17 and 18 and indicate that several phases are present. Specific minerals were identified later during the microprobe elemental mapping.

Culebra Dolomite

The Culebra dolomite appears to be a single phase rock with very minor amounts of other minerals present, as seen in Figure 19. The X-ray diffraction data also indicates dolomite as the major mineral phase.

ELECTRON MICROPROBE ELEMENTAL MAPPING

Westerly Granite (Figures 20 through 25)

The major elements found in areas A, B and C shown in the optical photographs were examined by elemental mapping with the electron microprobe. The electron scattering photograph, for example, shows area A from a somewhat different orientation than the area A in the optical photographs, but are otherwise the same areas. An electron scattering photograph is obtained by a method very similar to that used in electron microscopy. The photographs of the elements are at the same magnification and sample area as the electron scattering photograph. Each white dot represents a count of a characteristic X-ray emitted by the indicated element, and are directly proportional in density to the concentration of that element present in the upper few angstroms of the polished mount surface under observation. The density of white dots is thus a semiquantitative measure of the concentration of a given element.

By mentally superimposing the elemental X-ray emissions for a given crystal it is possible to make a reasonable guess as to the identity of the crystal mineral phase. For example, there are three high reflectivity crystals in the lower left quadrant of the area A electron scattering photograph. The largest crystal essentially contains only iron, and is either hematite or magnetite. The medium sized crystal contains both iron and titanium, and is either ilmenite or titaniferous magnetite. The smallest crystal contains calcium, iron, aluminum and silicon, and is presumably a garnet. Other probable minerals present in area A include a

MAGENTA DOLOMITE

FIGURE 17.

B 200X

C 200X

MAGENTA DOLOMITE

FIGURE 18.

CULEBRA DOLOMITE

FIGURE 19.

Electron Scattering 200X

Al

Ca

Fe

K

WESTERLY GRANITE
(A)

FIGURE 20.

Mg

Si

Ti

Zr

WESTERLY GRANITE

(A)

FIGURE 21.

Electron Scattering 200X

Al

Ca

Fe

K

WESTERLY GRANITE
(B)

FIGURE 22.

Mg

P

S

Si

WESTERLY GRANITE
(B)

FIGURE 23.

Electron Scattering 200X

Al

Ca

Fe

**WESTERLY GRANITE
(C)**

FIGURE 24.

K

P

Si

**WESTERLY GRANITE
(C)**

FIGURE 25.

biotite mica between crystals of orthoclase or microcline and a low calcium (and presumably a high sodium) plagioclase feldspar. There is also a small zircon crystal present on the lower edge of the potassium feldspar crystal.

Area B photographs show coincidental iron and sulfur areas, probably present as pyrite, and calcium and phosphorus areas as apatite. The just-visible fragment in the upper right electron scattering photograph quadrant is composed of plagioclase and a potassium feldspar.

Area C shows an area composed of patches of potassium feldspar, calcite, apatite and garnet in a plagioclase feldspar crystal.

Argillaceous Shale (Figures 26 through 31)

From the X-ray diffraction tracings, the illitic-kaolinitic fine matrix of this shale are known. Many small crystals of calcite, quartz and probably potassium feldspar can be located in all three areas. Coincidental iron and sulfur in area A probably indicate the presence of some pyrite. A fragment of apatite can be seen in area B in the calcium and phosphorus photographs. A dolomite fragment can be located in the calcium and magnesium photographs of area C.

Oolitic Limestone (Figures 32 through 36)

Small amounts of quartz and pyrite occurred in areas A, B and C, but the limestone was generally a relatively monomineralic (calcite) rock.

Sentinel Gap Basalt (Figures 37 through 40)

The main mineral phases comprising basalt can be easily discerned in area A and B photographs of element X-ray emissions. The aluminum photograph readily outlines the lath-like crystals of plagioclase. The calcium emissions photograph also outlines the plagioclase, but shows the pyroxenes as well. The magnesium photograph better outlines the pyroxenes without interference from other mineral phases. The magnetite, titaniferous magnetite and ilmenite are identifiable in the iron and titanium emission photographs. Pyroxenes also occur in the iron

Electron Scattering 100X

Al

Ca

Fe

**ARGILLACEOUS SHALE
(A)**

FIGURE 26.

K

Mg

S

Si

ARGILLACEOUS SHALE

(A)

FIGURE 27.

Electron Scattering 100X

Al

Ca

Fe

K

ARGILLACEOUS SHALE
(B)

FIGURE 28.

FIGURE 29.

Electron Scattering 100X

Al

Ca

Fe

K

ARGILLACEOUS SHALE
(C)

FIGURE 30.

Mg

Si

Ti

ARGILLACEOUS SHALE

(C)

FIGURE 31.

Electron Scattering 100X

Al

Ca

Fe

K

OOLITIC LIMESTONE
(A)

FIGURE 32.

Mg

P

S

Si

OOLITIC LIMESTONE

(A)

FIGURE 33.

FIGURE 34.

Electron Scattering 100X

Al

Ca

Fe

**OOLITIC LIMESTONE
(C)**

FIGURE 35.

K

Mg

Si

**OOLITIC LIMESTONE
(C)**

FIGURE 36.

Electron Scattering 100X

Al

Ca

Fe

SENTINEL GAP

A

FIGURE 37.

K

Mg

Si

Ti

SENTINEL GAP

A

FIGURE 38.

Electron Scattering 200X

Al

Ca

Fe

SENTINEL GAP

B

FIGURE 39.

K

Mg

Si

Ti

SENTINEL GAP

B

FIGURE 40.

photograph, but usually contain less total iron than the metallic oxides. Silicon occurs through all of the minerals except the metallic oxides, and through the groundmass. The groundmass is relatively high in potassium content. Hence, the potassium emissions photograph can be used to gauge the areal extent of the basalt groundmass. In the case of basalts, the groundmass usually contains those elements that did not fit well into the main stage mineral phases. Potassium is one of the left-over elements.

Conasauga Shale (Figures 41 through 44)

The Conasauga shale includes rather large quartz fragments that can be seen in the silicon photograph of both area B and C. Coincidental iron and sulfur emission areas indicate the probable presence of pyrite in area B. A smaller amount of sulfide occurs in area C. The fine matrix was composed of illite and kaolinite according to X-ray diffraction tracings. There is an irregular area of apatite in area B as evidenced by coincidental calcium and phosphorus emissions. The apatite probably originated from a nondetrital source because of its highly irregular shape. A detrital apatite crystal would tend to be more compact and regular in shape.

Climax Stock Granite (Figures 45 through 48)

Several mineral phases can be tentatively identified in area A including biotite, potassium feldspar, plagioclase, quartz, apatite, rutile, sphene, and magnetite or hematite. Most of the same minerals can be identified in area B as well. Though the Climax Stock material has generally been referred to as a granite, Houser and Poole (1961) pointed out that the stock varied from a granodiorite to a quartz monzonite in composition. Feldspar quantitative relations will be determined in a following section as a basis for classification of the standard rock sample.

Anhydrite (Figures 49 through 52)

Area A, and to a lesser extent area B, show the presence of a considerable quantity of magnesium in areas that are calcium-free and sulfur-free. In the apparent absence of an accompanying anion, the anion

Electron Scattering 100X

Al

Ca

Fe

**Conasauga
Area - B**

FIGURE 41

K

Mg

P

S

Si

Ti

**Conasauga
Area-B**

FIGURE 42.

Electron Scattering 100X

Al

Ca

Fe

**Conasauga
Area-C**

FIGURE 43.

**Conasauga
Area-C**

FIGURE 44.

Electron Scattering 100X

Al

Ca

Fe

**Climax Granite
Area-A**

FIGURE 45.

**Climax Granite
Area-A**

FIGURE 46.

Electron Scattering 100X

Al

Ca

Fe

**Climax Granite
Area - B**

FIGURE 47.

**Climax Granite
Area-B**

FIGURE 48.

Electron Scattering 100X

Al

Ca

**Anhydrite
Area-A**

FIGURE 49.

Fe

Mg

S

Si

**Anhydrite
Area-A**

FIGURE 50.

Electron Scattering 100X

Al

Ca

Fe

**Anhydrite
Area-B**

FIGURE 51.

K

Mg

S

Si

**Anhydrite
Area-B**

FIGURE 52.

is probably carbonate. Thus the magnesium compound is probably magnesite. Approximately 25 to 30% of area A is magnesite, but less than 10% of area B. The whole-rock chemical analysis of Table 5 can be used to estimate the overall magnesite content of the anhydrite since dolomite is absent from the rock.

Magenta Dolomite (Figures 53 through 56)

The Magenta dolomite sample is mostly composed of gypsum, as shown by the X-ray diffraction tracings and by the sulfur emissions in area B and especially in area C that is essentially all gypsum except for a few quartz grains and small dolomite areas. The electron scattering photograph of area B shows the gypsum area as white in color and the dolomite area as dark gray.

Culebra Dolomite (Figures 57 through 60)

The Culebra dolomite is apparently all dolomite except for a few scattered grains of quartz and potassium feldspar. A small siderite crystal can be seen in the upper left quadrant of area C. The X-ray emission photographs exaggerate somewhat the actual size of such small crystals because the X-ray emissions are in three dimensions rather than two. The nonperpendicular emissions tend to spread sideways on the oscilloscope and film, yielding a larger apparent crystal fragment on the photograph than the actual crystal fragment.

Electron Scattering 100X

Al

Ca

Fe

**Magenta Dolomite
Area - B**

FIGURE 53.

K

Mg

S

Si

**Magenta Dolomite
Area- B**

FIGURE 54.

Electron Scattering 100X

Al

Ca

Fe

**Magenta Dolomite
Area-C**

FIGURE 55.

K

Mg

S

Si

**Magenta Dolomite
Area-C**

FIGURE 56.

Electron Scattering 100X

Al

Ca

Fe

Culebra Dolomite

Area-B

FIGURE 57.

K

Mg

Si

Ti

Culebra Dolomite

Area-B

FIGURE 58.

Electron Scattering 100X

Al

Ca

**Culebra Dolomite
Area-C**

FIGURE 59.

Fe

K

Mg

Si

**Culebra Dolomite
Area-C**

FIGURE 60.

ELECTRON MICROPROBE CHEMICAL ANALYSIS

Westerly Granite

The microprobe chemical analyses and the mineral compositions and identifications derived from them are given in Table 6. The dashes indicate that the constituent was below the microprobe analytical limits, usually 0.1 wt%. Both the major mineral constituents such as quartz, potassium feldspar, oligoclase and biotite were determined as well as the minor constituents such as zircon, allanite, apatite, calcite and chalcopyrite that may directly or indirectly affect certain of the radionuclide distribution coefficients. The minor mineral phases are present at less than 5% by weight, and usually less than 1% by weight. However, the minor mineral phases could influence radionuclide distributions or adsorption out of proportion to their actual concentration in the rock. For example, the chalcopyrite may lower Eh values, calcite could increase the pH and allanite might contribute a relatively large concentration of thorium and rare earths to an equilibrating solution. The effects of these events on radionuclide adsorption under certain circumstances could be quite large. Thus comprehensive attempts to identify trace mineral constituents is probably warranted.

The computations, based directly on the chemical analyses, were carried out to two places past the decimal point. The elements or groups of elements with only a single number for a subscript are either the oxygen values on which the cation numbers were based, or constitute a reasonable estimate of the mineral or minerals represented by the chemical analysis. For example, calcite was deduced from the reported CaO values in analysis 16 and magnetite was deduced from the wt% FeO given in analysis 10 of Table 7. These are estimates, not absolute determinations because carbonate could not be determined in analysis 16, or the ferrous to ferric iron ratio in analysis 10. In analysis 14, only the sum of thorium, lanthanum and cerium were reported, but the analysis is very similar to known allanite compositions (Deer, Howie and Zussman, 1962a, p. 214). Analysis 18 is high due to reporting of the iron as the oxide.

TABLE 7. Microprobe Chemical Analyses and Computed Compositions of Minerals in the 20 to 50 Mesh Westerly Granite.

	Wt%																	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
SiO ₂	67.3	65.9	61.6	63.9	62.8	63.9	100.4	101.1	0.2	0.2	0.9	0.5	39.0	32.5	39.0	0.2	32.9	--
Al ₂ O ₃	17.7	20.9	17.3	20.9	20.6	17.2	--	--	0.2	--	--	--	14.5	12.1	21.4	0.3	0.2	--
TiO ₂	--	--	--	--	--	--	--	--	47.1	--	--	--	2.5	1.1	--	--	0.2	--
BaO	0.3	--	0.4	--	--	0.5	--	--	--	--	--	--	0.9	--	--	0.1	--	--
CaO	--	4.0	--	3.2	3.9	--	--	--	0.3	--	61.0	59.6	--	12.9	28.4	57.3	--	0.3
MgO	--	--	--	--	--	--	--	--	0.2	0.2	0.2	0.3	8.5	0.4	--	--	--	--
FeO	0.1	--	--	--	--	--	--	--	44.2	90.0	--	0.2	19.3	10.0	11.6	0.4	--	38.4
MnO	--	--	--	--	--	--	--	--	4.4	--	--	--	--	0.3	--	--	--	--
CrO ₃	--	--	--	--	--	--	--	--	--	0.2	--	--	--	--	--	--	--	--
S	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	34.7
ZrO ₂	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	65.8	--
HfO ₂	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	1.3	--
K ₂ O	16.6	--	17.4	0.2	0.1	17.2	--	--	--	--	--	--	11.2	0.3	--	--	0.6	0.7
Na ₂ O	--	8.6	--	8.8	8.3	--	--	--	--	--	--	--	--	--	--	--	--	--
Cu	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	33.2
La, Ce, Th	--	--	--	--	--	--	--	--	--	--	--	--	--	30.0	--	--	--	--
P ₂ O ₅	--	--	--	--	--	--	--	--	--	--	41.0	39.7	--	--	--	0.2	--	--
TOTAL	102.0	99.6	96.7	97.0	95.7	98.8	100.4	101.1	96.8	90.6	103.1	100.3	95.9	99.6	100.4	58.5	101.0	107.3
	Composition						Mineralogy						Composition					
1. (K _{3.84})(Al _{3.78} Si _{12.20})O ₃₂							Orthoclase or microcline						10. 96.7 wt% Fe ₃ O ₄					
2. (Na _{2.94} Ca _{0.75})(Al _{4.35} Si _{11.63})O ₃₂							Oligoclase						11. (Ca,Mg,Fe) _{5.60} (PO ₄) _{3.00} (OH) ₂					
3. (K _{4.30})(Al _{3.95} Si _{11.96})O ₃₂							Orthoclase or microcline						12. (Ca,Mg,Fe) _{5.60} (PO ₄) _{3.00} (OH) ₂					
4. (Na _{3.09} Ca _{0.62})(Al _{4.46} Si _{11.57})O ₃₂							Oligoclase						13. K _{2.40} (Mg _{2.12} Fe _{2.71})(Al _{2.43} Ti _{0.31})(Al _{0.43} Si _{7.57})O ₂₂ (OH) ₂					
5. (Na _{2.96} Ca _{0.77})(Al _{4.45} Si _{11.53})O ₃₂							Oligoclase						14. (Ca,Mn,Mg,Ce,La,Th) ₂ (Fe,Ti)(Al,Fe) ₂ (Si ₃ O ₁₂)OH					
6. (K _{4.14})(Al _{3.83} Si _{12.09})O ₃₂							Orthoclase or Microcline						15. (Fe _{1.49} Ca _{4.68})(Al _{3.89})(Si _{6.00})O ₂₄					
7. SiO ₂							Quartz						16. 102.3 wt% CaCO ₃					
8. SiO ₂							Quartz						17. (Zr _{3.96} Hf _{0.04})(Si _{4.08})O ₁₆					
9. (Fe) _{2.06} (Ti) _{2.00} O ₆							Ilmenite						18. Cu _{0.98} Fe _{1.00} S _{2.03}					

Note: The dashes indicate that constituent was below detection limits.

Analysis 10 is low because the iron is probably present as Fe_3O_4 rather than FeO , and analysis 16 is low because no anion was found.

Argillaceous Shale

The microprobe chemical analyses and mineral compositions derived from them for the 20 to 50 mesh argillaceous shale are shown in Table 8. The matrix compositions, analyses 1, 2 and 3, are reasonable estimates of the shale matrix composition based on X-ray diffraction tracings and on known illite compositions (Deer, Howie and Zussman, 1962b, p. 219). Analysis 12 shows that considerable excess sulfur is present as well as pyrite. Analyses 9, 10 and 11 are all low due to the lack of anions. The calcium, magnesium and iron were all computed as carbonates.

Oolitic Limestone

The microprobe chemical analyses of the 20 to 50 mesh oolitic limestone and derived mineral compositions are presented in Table 9. There are not many minerals contaminating the calcite making up the bulk of this relatively pure rock. A small amount of quartz and pyrite are the only contaminating minerals.

Sentinel Gap Basalt

The microprobe chemical analyses and derived mineral compositions for the 20 to 50 mesh Sentinel Gap basalt are shown in Table 10. Sentinel Gap designates the geographic location from which the basalt was collected. There are several flow units that can be found in Sentinel Gap, including this basalt sample from the flow unit immediately above the Untanum, none of which bear the geologic name of Sentinel Gap basalt.

The feldspar compositions are not far from the andesine-laboradorite field boundary, while the pyroxenes are mainly augites with an occasional ferroaugite or pigeonite. The metallic oxides are titaniferous magnetite and ilmenite. The titaniferous magnetites do not correspond in composition to any metallic oxide. Likewise, the olivene has lost magnesium and does not exactly correspond to an olivine composition. A good dioctahedral smectite composition was determined from analysis 11 results. The clay mineral could be referred to as a nontronite. The groundmass, or residual liquid of the flow was glassy with many

TABLE 8. Microprobe Chemical Analyses and Computed Compositions of Minerals in the 20 to 50 Mesh Argillaceous Shale

	Wt%												
	1	2	3	4	5	6	7	8	9	10	11	12	13
SiO ₂	61.0	61.6	58.8	94.2	101.7	100.9	65.8	65.5	1.1	3.3	1.5	0.9	0.1
Al ₂ O ₃	23.6	21.1	22.2	3.6	--	--	17.3	16.9	0.3	0.8	--	0.3	--
TiO ₂	0.3	1.7	0.6	--	--	--	--	--	--	--	0.1	--	--
BaO	--	--	--	--	--	--	0.4	--	--	--	--	--	--
CaO	0.1	0.3	2.0	--	--	--	--	--	33.7	33.9	36.6	--	55.0
MgO	1.2	1.6	2.8	--	--	--	--	--	17.0	17.7	19.2	0.3	0.5
FeO	3.7	4.8	4.7	0.7	0.2	0.2	0.3	0.3	6.4	2.6	1.9	43.8	0.2
K ₂ O	11.3	8.0	8.6	1.8	0.2	--	17.7	17.4	0.3	0.3	0.4	0.7	--
Na ₂ O	--	--	--	--	--	--	--	--	--	--	--	--	--
P ₂ O ₅	--	--	--	--	--	--	--	--	0.1	--	0.3	--	44.4
S	--	--	--	--	--	--	--	--	--	0.3	--	51.4	--
TOTAL	101.2	99.1	99.7	100.3	102.1	101.1	101.0	100.1	58.9	58.9	60.0	97.4	100.2

Composition	Mineralogy
1. Matrix; mainly $KAl_4(Si_7,Al)O_{20}(OH)_4$	Illite
2. Matrix; mainly $KAl_4(Si_7,Al)O_{20}(OH)_4$	Illite
3. Matrix; mainly $KAl_4(Si_7,Al)O_{20}(OH)_4$	Illite
4. SiO ₂	Quartz
5. SiO ₂	Quartz
6. SiO ₂	Quartz
7. $(K)_{4.12}(Al_{3.76},Si_{12.14})O_{32}$	Microcline or orthoclase
8. $(K)_{4.16}(Al_{3.71},Si_{12.19})O_{32}$	Microcline or orthoclase
9. $(Ca_{0.54},Mg_{0.38},Fe_{0.08})CO_3$	Dolomite, calcite, siderite
10. $(Ca_{0.56},Mg_{0.41},Fe_{0.03})CO_3$	Dolomite, calcite, siderite
11. $(Ca_{0.57},Mg_{0.41},Fe_{0.02})CO_3$	Dolomite, calcite, siderite
12. FeS _{2.62}	Pyrite, sulfur
13. $(Ca,Fe,Mg)_{4.80}(PO_4)_{3.00}(OH)_2$	Apatite

Note: The dashes indicate that constituent was below detection limits.

TABLE 9. Microprobe Chemical Analyses and Computed Compositions of Minerals in the 20 to 50 Mesh Oolitic Limestone

	Wt%					
	1	2	3	4	5	6
SiO ₂	---	---	---	0.9	102.0	99.7
Al ₂ O ₃	---	---	---	---	---	---
TiO ₂	---	---	---	---	---	---
CaO	56.8	56.8	56.1	0.9	0.8	1.0
MgO	0.5	0.9	0.2	0.1	---	---
FeO	---	---	---	55.2	---	---
K ₂ O	---	---	---	---	---	---
Na ₂ O	---	---	---	---	---	---
P ₂ O ₅	0.2	0.2	0.2	---	---	---
S	---	---	---	52.6	---	---
TOTAL	57.5	57.9	56.5	109.8	102.8	100.7

	Composition	Mineralogy
1.	CaCO ₃	Calcite
2.	CaCO ₃	Calcite
3.	CaCO ₃	Calcite
4.	Fe _{1.00} S _{2.09}	Pyrite
5.	SiO ₂	Quartz
6.	SiO ₂	Quartz

Note: The dashes indicate that constituent was below detection limits.

TABLE 10. Microprobe Chemical Analyses and Computer Compositions of Minerals in the 20 to 50 Mesh Sentinel Gap Basalt

	Wt%												
	1	2	3	4	5	6	7	8	9	10	11	12	13
SiO ₂	60.5	58.7	49.4	52.6	46.9	51.8	36.4	0.2	0.2	0.3	55.3	76.3	76.9
Al ₂ O ₃	24.4	26.1	0.8	1.1	1.0	0.9	--	0.2	0.9	2.2	6.3	12.9	11.6
TiO ₂	--	--	0.6	0.4	0.6	0.4	--	51.8	27.9	28.1	0.1	0.7	--
FeO	0.9	0.8	21.6	11.5	17.0	29.8	52.0	45.5	68.8	68.4	27.6	1.9	1.4
MnO	--	--	0.4	0.2	0.2	0.5	0.7	0.4	0.3	0.4	--	--	--
CaO	9.3	11.9	11.9	19.1	20.2	8.2	0.4	--	--	--	1.3	0.5	0.4
MgO	--	--	12.1	15.1	11.3	8.3	12.1	--	0.5	1.4	5.0	--	--
K ₂ O	0.9	0.5	--	--	--	--	--	--	--	--	0.6	6.9	6.5
Na ₂ O	5.8	4.7	--	--	--	--	--	--	--	--	--	--	--
P ₂ O ₅	--	--	--	--	--	--	--	--	--	--	--	--	--
TOTAL	101.8	102.7	96.8	100.0	97.2	99.9	101.6	98.1	98.6	100.8	96.2	99.2	96.8

Composition	Mineralogy
1. (Na _{1.99} ,Ca _{1.77} ,K _{0.20})(Al _{5.11} ,Si _{10.74})O ₃₂	Andesine
2. (Na _{1.62} ,Ca _{2.26} ,K _{0.12})(Al _{5.45} ,Si _{10.40})O ₃₂	Labradorite
3. (Mg _{0.72} ,Fe _{0.72} ,Ca _{0.51} ,Ti _{0.02} ,Mn _{0.01} ,Al _{0.03})(Al _{0.03} ,Si _{1.97})O ₆	Augite
4. (Mg _{0.84} ,Fe _{0.36} ,Ca _{0.77} ,Ti _{0.01} ,Mn _{0.01} ,Al _{0.02})(Al _{0.03} ,Si _{1.97})O ₆	Augite
5. (Mg _{0.68} ,Fe _{0.57} ,Ca _{0.87} ,Ti _{0.02} ,Mn _{0.01})(Al _{0.05} ,Si _{1.88})O ₆	Augite
6. (Mg _{0.47} ,Fe _{0.95} ,Ca _{0.33} ,Ti _{0.01} ,Mn _{0.02} ,Al _{0.04})(Si _{1.96})O ₆	Subcalcic ferroaugite
7. ---	Altered olivine
8. (Fe,Mn) _{1.98} (Ti) _{2.00} O ₆	Ilmenite
9. ---	Titaniferous magnetite
10. ---	Titaniferous magnetite
11. (Al _{0.15} ,Mg _{0.49} ,Fe _{1.53})(Al _{0.34} ,Si _{3.66})O ₁₀ (OH) ₂	Diocahedral smectite largely nontronite
12. Ground-mass	Microcrystalline feldspar in a rhyolitic glassy matrix
13. Ground-mass	

Note: The dashes indicate that constituent was below detection limits.

crystallites of feldspar. Overall, the groundmass is rhyolitic in composition with high silica and potassium contents. Other constituents such as iron, calcium, magnesium and sodium tended to be low due to removal during main stage crystallization.

Conasauga Shale

The microprobe chemical analyses and computed mineral compositions in the 20 to 50 mesh Conasauga shale are given in Table 11. The fine grained matrix analyses shown in 1, 2 and 3 represent a range in a composition, with the mineral composition an estimate based on the X-ray diffraction results and chemical analyses. Quartz is the prevalent large mineral found in the matrix of illite and kaolinite although pyrite, apatite, andesine, calcite and occasional zircons also can be found.

Climax Stock Granite

The microprobe chemical analyses and computed compositions of the minerals in the 20 to 50 mesh Climax Stock granite are given in Table 12. As can be seen in Table 12, the feldspar accompanying the potassium feldspar is an andesine. This is too calcic a plagioclase, and there is too much of it to classify the Climax Stock material as a granite. It would more aptly be referred to as a granodiorite than granite.

The hastingsite is a hornblende that occurs in a wide variety of igneous and metamorphic rocks, and contains a considerable amount of ferrous iron (Deer, Howie, and Zussman, 1963, p. 288), as does the biotite. Some Eh buffering could be expected from these minerals and from the magnetite.

Anhydrite

The microprobe chemical analyses and derived mineral compositions for the 20 to 50 mesh anhydrite are given in Table 13. Though no carbonate was directly determined by the microprobe, the magnesium compound is almost certainly magnesite. The presence of a sizable amount of carbonate buffers the pH of any solution contacting the anhydrite to a relatively basic level. Water was not determined on the microprobe, so positive gypsum identifications could not be made by this method. A small water

TABLE 11. Microprobe Chemical Analyses and Computed Compositions of Minerals in the 20 to 50 Mesh Conasauga Shale

	Wt%									
	1	2	3	4	5	6	7	8	9	10
SiO ₂	21.3	55.2	63.2	98.9	0.9	35.9	98.1	0.5	5.9	59.9
Al ₂ O ₃	16.3	25.8	20.5	---	0.3	---	---	0.1	4.9	23.7
TiO ₂	29.9	0.5	1.8	---	---	---	---	---	---	---
CaO	0.1	0.3	0.3	---	52.5	---	---	52.1	0.2	6.7
MgO	2.9	2.2	1.1	---	0.8	---	---	0.5	1.3	---
FeO	28.5	9.7	5.1	0.1	2.2	---	0.3	0.6	46.7	0.4
K ₂ O	2.2	7.2	6.6	---	0.1	---	---	---	---	0.1
Na ₂ O	---	---	---	---	---	---	---	---	---	7.9
ZrO ₂	---	---	---	---	---	59.1	---	---	---	---
HfO ₂	---	---	---	---	---	1.2	---	---	---	---
P ₂ O ₅	---	---	0.2	---	0.2	---	---	43.2	---	---
S	---	---	---	---	---	---	---	---	40.5	---
TOTAL	101.2	100.9	98.8	99.0	57.0	96.2	98.4	98.4	99.5	98.7

	Composition	Mineralogy
1.	Matrix; FeTiO ₃ , KA ₁ (Si ₇ , Al) ₀ 20(OH) ₄	Ilmenite, illite
2.	Matrix; KA ₁ (Si ₇ , Al) ₀ 20(OH) ₄ , Fe ₂ O ₃	Illite, hematite
3.	Matrix; Al ₄ Si ₄ O ₁₀ (OH) ₈ , KA ₁ (Si ₇ , Al) ₀ 20(OH) ₄	Kaolinite, illite
4.	SiO ₂	Quartz
5.	Mainly CaCO ₃	Calcite
6.	(Zr _{0.98} , Hf _{0.001})(Si _{1.17}) ₀ 4	Zircon
7.	SiO ₂	Quartz
8.	(Ca, Mg, Fe) _{4.80} (PO ₄) _{3.00} (OH) ₂	Apatite
9.	Fe S _{1.95}	Pyrite
10.	(Na _{2.78} , Ca _{1.30}) (Al _{5.06} , Si _{10.86}) ₀ 32	Andesine

Note: The dashes indicate that constituent was below detection limits.

TABLE 12. Electron Microprobe Chemical Analyses and Computed Compositions of Minerals in the 20 to 50 Mesh Climax Stock Granite

	Wt%												
	1	2	3	4	5	6	7	8	9	10	11	12	13
SiO ₂	98.1	98.3	56.6	57.6	63.5	0.5	0.3	0.2	6.0	30.7	30.5	35.2	34.1
Al ₂ O ₃	--	--	24.8	24.9	18.3	0.1	--	--	0.6	1.8	2.4	20.0	14.0
TiO ₂	--	--	--	--	--	--	0.2	0.1	0.6	32.7	32.9	3.0	2.8
BaO	--	--	--	--	0.2	--	--	--	--	--	--	--	--
CaO	--	--	8.7	9.3	--	55.1	54.1	--	0.6	31.8	32.4	25.0	--
MgO	--	--	--	--	--	0.6	0.2	0.5	1.4	0.8	0.3	0.8	10.6
FeO	--	--	--	0.2	0.1	0.8	0.1	86.2	93.2	1.7	2.7	13.9	28.8
K ₂ O	--	--	0.3	0.4	16.3	--	--	--	0.1	--	--	0.2	10.5
NaO	--	--	6.8	6.3	--	--	--	--	--	--	1.3	--	--
P ₂ O ₅	--	--	--	--	--	43.8	44.6	--	--	--	0.2	--	--
CrO ₃	--	--	--	--	--	--	--	--	0.1	--	--	--	--
MnO	--	--	--	--	--	--	--	--	0.5	--	--	--	--
TOTAL	98.1	98.3	97.2	98.7	98.4	100.9	99.5	87.0	103.1	99.5	102.7	98.1	100.8

Composition	Mineralogy
1. SiO ₂	Quartz
2. SiO ₂	Quartz
3. (Na _{2.43} ,Ca _{1.72} ,K _{0.01})(Al _{5.40} ,Si _{10.46})O ₃₂	Andesine feldspar
4. (Na _{2.23} ,Ca _{1.82} ,K _{0.01})(Al _{5.35} ,Si _{10.52})O ₃₂	Andesine feldspar
5. (K _{3.92})(Al _{4.06} ,Si _{11.97})O ₃₂	Microcline or orthoclase
6. (Ca,Mg,Fe) _{5.00} (PO ₄) _{3.00} (OH) ₂	Apatite
7. (Ca,Mg,Fe) _{4.80} (PO ₄) _{3.00} (OH) ₂	Apatite
8. 95.8 wt% Fe ₂ O ₃	Hematite
9. 100.1 wt% Fe ₃ O ₄	Magnetite
10. Ca _{1.09} Ti _{0.78} Si _{1.00} O ₅	Sphene
11. Ca _{1.09} Ti _{0.78} Si _{1.00} O ₅	Sphene
12. (K _{0.04} ,Ca _{2.66})(Ca _{1.63} ,Al _{1.40} ,Ti _{0.37} ,Mg _{0.19} ,Fe _{1.86})(Si _{5.63} ,Al _{2.37}) ₂ (OH,F) ₂	Hastingsite
13. K _{2.24} (Mg _{2.64} ,Fe _{3.36})(Fe _{0.68} ,Al _{0.45} ,Ti _{0.35})(Si _{5.69} ,Al _{2.31})O ₂₄ (OH) ₂	Biotite

Note: The dashes indicate that constituent was below detection limits.

TABLE 13. Microprobe Chemical Analyses and Computed Compositions of Minerals in the 20 to 50 Mesh Anhydrite

	Wt%			
	1	2	3	4
SiO ₂	---	0.1	---	0.6
Al ₂ O ₃	0.1	---	---	---
CaO	40.2	1.2	40.6	0.2
MgO	0.3	46.9	0.4	48.1
FeO	---	---	---	---
K ₂ O	---	---	---	---
Na ₂ O	---	---	---	---
SO ₃	54.8	0.6	54.9	---
TOTAL	95.4	48.8	95.9	48.9

Composition	Mineralogy
1. Ca _{1.00} (SO ₄) _{0.96}	Anhydrite or gypsum
2. 98.1 wt% MgCO ₃	Magnesite
3. Ca _{1.00} (SO ₄) _{0.95}	Anhydrite or gypsum
4. 100.6 wt% MgCO ₃	Magnesite

Note: The dashes indicate that constituent was below detection limits.

loss reported in Table 5 chemical analysis showed that the bulk of this rock is anhydrite.

Magenta Dolomite

The microprobe chemical analyses and derived mineral compositions for the 20 to 50 mesh Magenta dolomite are given in Table 14. Though the microprobe does not determine water content, the X-ray diffraction tracings show the presence of gypsum, but no anhydrite. The amount of dolomite in relation to gypsum was rather small in the X-ray tracing so that the designation of this rock as a dolomite is somewhat misleading. However, the sedimentary chemical precipitates are well-known for their nonhomogeneity, and such mineral variations are not unusual.

TABLE 14. Microprobe Chemical Analyses and Computed Compositions of Minerals in the 20 to 50 Mesh Magenta Dolomite

	Wt%						
	1	2	3	4	5	6	7
SiO ₂	99.3	0.3	0.2	---	98.6	0.2	---
Al ₂ O ₃	---	---	0.3	---	---	---	0.1
TiO ₂	---	---	---	---	---	---	---
CaO	0.3	42.5	50.7	30.3	---	46.0	29.7
MgO	---	---	1.2	23.4	---	0.3	20.1
FeO	---	---	---	---	---	---	---
K ₂ O	---	---	---	---	---	---	---
Na ₂ O	---	---	---	---	---	---	---
SO ₃	---	55.6	44.8	---	---	51.1	---
TOTAL	99.6	98.4	97.2	53.7	98.6	97.6	49.9

	Composition	Mineralogy
1.	SiO ₂	Quartz
2.	Ca _{1.00} (SO ₄) _{0.94}	Anhydrite or gypsym
3.	68.8 wt% CaSO ₄ + 31.2 wt% CaCO ₃	Anhydrite or gypsum, calcite
4.	(CaCO ₃) _{1.00} (MgCO ₃) _{1.07}	Dolomite
5.	SiO ₂	Quartz
6.	82.7 wt% CaSO ₄ + 17.3 wt% CaCO ₃	Anhydrite or gypsum, calcite
7.	(CaCO ₃) _{1.00} (MgCO ₃) _{0.94}	Dolomite

Note: The dashes indicate that constituent was below detection limits.
Culebra Dolomite

The microprobe chemical analyses and derived mineral compositions for the 20 to 50 mesh Culebra dolomite are given in Table 15. The CaO and MgO values reported from the microprobe work were computed as dolomites because the X-ray data indicated that greater than 90% of the rock was composed of dolomite. An occasional very small detrital particle of quartz, potassium feldspar or rutile were the only other minerals observed in the Culebra dolomite sample.

TABLE 15. Microprobe Chemical Analyses and Computed Compositions of Minerals in the 20 to 50 Mesh Culebra Dolomite

	Wt%						
	1	2	3	4	5	6	7
SiO ₂	---	---	---	0.1	62.2	0.1	96.2
Al ₂ O ₃	---	---	---	---	18.5	0.3	---
TiO ₂	---	---	---	---	---	84.0	---
CaO	30.5	31.5	32.3	31.5	---	10.2	2.2
MgO	21.2	21.0	21.3	21.3	---	3.6	---
FeO	---	---	---	---	---	---	---
K ₂ O	---	---	---	---	16.9	---	---
Na ₂ O	---	---	---	---	---	---	---
TOTAL	51.7	52.5	53.6	52.8	97.9	98.2	98.4
Composition				Mineralogy			
1. (CaCO ₃) _{1.00} (MgCO ₃) _{0.99}				Dolomite			
2. (CaCO ₃) _{1.04} (MgCO ₃) _{0.96}				Dolomite			
3. (CaCO ₃) _{1.04} (MgCO ₃) _{0.96}				Dolomite			
4. (CaCO ₃) _{1.02} (MgCO ₃) _{0.97}				Dolomite			
5. (K) _{4.10} (Al _{4.15} , Si _{11.86}) _{0.32}				Microcline or orthoclase			
6. Chiefly TiO ₂ , some CaCO ₃ , MgCO ₃				Rutile, some calcite, dolomite			
7. SiO ₂ , small amount of CaCO ₃				Quartz, minor calcite			

Note: The dashes indicate that constituent was below detection limits.

B.E.T. SURFACE AREA

The B.E.T. surface areas, measured on the Micromeritics Model 2200 (nitrogen) and Model 2205 (argon) Surface Area Analyzers, are given in Table 16. The shales with the largest fractions of fine-grained materials are highest in B.E.T. surface area. The B.E.T. gas absorption method supposedly measures external surface area only, although an exact definition of external surface area was not given (Haynes, 1961).

TABLE 16. B.E.T. Surface Areas of the 20 to 50 Mesh
Standard Rock Samples

<u>Rock</u>	<u>Surface Area, m²/g</u>
Westerly Granite	0.11
Argillaceous Shale	20.7
Oolitic Limestone	0.75
Sentinel Gap Basalt	2.5
Conasauga Shale	7.2
Climax Stock Granite	0.08
Anhydrite	0.63
Magenta Dolomite	2.5
Culebra Dolomite	2.0

ETHYLENE GLYCOL SORPTION SURFACE AREA

The glycol surface areas, measured by a weight method described in Rai and Franklin (1978, in press), are listed in Table 17. The plus or minus values following the mean surface areas are standard deviations determined in triplicate surface area measurements. The ethylene glycol sorption surface areas average five to seven times the B.E.T. surface area values, probably due to the measurement of both internal and external surface areas. However, the difference between external and internal area is often difficult to define. In any case the glycol surface areas appear to correlate somewhat better with cation exchange capacity and radionuclide distribution coefficients than do the B.E.T. surface areas.

The relatively large surface area of the Magenta dolomite in Table 17 may be a result of its high gypsum content. Ethylene glycol, a highly polar molecule, may be able to partially replace the water molecules in gypsum, and hence yield a higher apparent surface area for gypsum than would be the case for anhydrite, for example, of the same mesh size range. In any case, the high surface area of the Magenta dolomite in Table 71 is suspect.

TABLE 17. Ethylene Glycol Sorption Surface Areas of the
20 to 50 Mesh Standard Rock Samples

<u>Rock</u>	<u>Surface Area,</u> <u>m²/g</u>	
	<u>Mean</u>	<u>Std.Dev.</u>
Westerly Granite	5.98	± 2.38
Argillaceous Shale	70.67	± 5.0
Oolitic Limestone	5.6	± 1.7
Sentinel Gap Basalt	10.3	± 1.0
Conasauga Shale	48.2	± 1.4
Climax Stock Granite	3.9	± 0.85
Anhydrite	5.5	± 1.06
Magenta Dolomite	136.97	± 9.06
Culebra Dolomite	9.91	± 2.07

STRONTIUM CATION EXCHANGE CAPACITY

The cation exchange capacities of the 20 to 50 mesh standard rock samples measured with ⁸⁵Sr are given in Table 18.

TABLE 18. Cation Exchange Capacities of the Standard 20 to 50 Mesh
Rock Samples Measured with Strontium

<u>Rock</u>	<u>Cation Exchange</u> <u>Capacity, meq/100 g</u>	
	<u>Mean</u>	<u>Std.Dev.</u>
Westerly Granite	4.4	± 0.1
Argillaceous Shale	9.8	± 1.3
Oolitic Limestone	42	± 16
Sentinel Gap Basalt	4.7	± 0.2
Conasauga Shale	6.2	± 0.8
Climax Stock Granite	0.85	± 0.19
Anhydrite	143	± 107
Magenta Dolomite	7.3	± 1.6
Culebra Dolomite	15.4	± 13

These values represent means of three capacity determinations, and are followed by their standard deviations.

The determination of cation exchange capacities of rocks with strontium solutions can be misleading when the rocks are chiefly made up of relatively soluble calcium minerals. Undoubtedly, the exchange capacity of the Oolitic limestone, for example, would be much lower if measured with cesium instead of strontium. There is some question as to the interpretation of cation exchange capacity results from a relatively water soluble compound such as gypsum or anhydrite. With the above reservations, the capacity data of Table 18 are useful for comparative purposes.

ESTIMATION OF QUANTITATIVE MINERALOGY

A quantitative estimation of the major minerals present in the standard rock is given in Table 19. Several methods were used for a modal analysis including use of the Quantimet on the Sentinel Gap basalt and computation from the whole rock chemical analyses in Table 5 for the Oolitic limestone, anhydrite, Magenta dolomite and Culebra dolomite. The modal analyses of the Climax Stock granite, Westerly granite, Argillaceous shale and Conasauga shale were determined petrographically with a microscopic examination of several areas in the rock sample mounts. The modal analyses were then recomputed to weight percent relationships using standard specific gravities for the minerals. The least reliable of the estimations shown in Table 19 are those for the Argillaceous and Conasauga shales due to their marked nonhomogeneity. The next least reliable quantitative mineralogy estimates were those for the Anhydrite, Magenta dolomite and Culebra dolomite. The quantitative estimates as given are reasonably good, but it would not be too difficult to remove a nonrepresentative sample from any of the above three standard rocks. Their mineralogy tends to vary considerably, as illustrated by the calcium and magnesium X-ray emission photographs of anhydrite areas A and B. The anhydrite fragment in area B contains much less magnesite than the anhydrite fragment shown in area A. The igneous standard rocks were more nearly homogeneous than the sedimentary rock standards and gave less trouble during the modal analysis.

TABLE 19. Quantitative Estimation of Minerals in the 20
to 50 Mesh Standard Rock Samples

<u>Rock</u>	<u>Major Minerals</u>	<u>wt%</u>
Westerly Granite	Oligoclase	34
	Microcline	33
	Quartz	25
	Biotite	5
	Magnetite	2
	Muscovite	1
Argillaceous Shale	Illite-Kaolinite	85
	Quartz	12
	Calcite	3
Oolitic Limestone	Calcite	99
	Clays	1
Sentinel Gap Basalt	Plagioclase (Ab ₅₅ -Ab ₄₀)	44
	Pyroxenes	32
	Groundmass	13
	Metallic Oxides	6
	Clays	5
Conasauga Shale	Illite-Kaolinite	52
	Quartz	35
	Andesine	10
	Pyrite	3
Climax Stock Granite	Andesine	47
	Quartz	28
	Microcline	15
	Biotite	10
Anhydrite	Anhydrite	72
	Magnesite	23
	Trona	5
Magenta Dolomite	Gypsum	56
	Dolomite	35
	Quartz	7
	Clays	2
Culebra Dolomite	Dolomite	96
	Clays	2
	Quartz	1
	Potassium Feldspar	1

PERTINENCE OF CHARACTERIZATION DATA TO Kd DETERMINATIONS

Several of the rock samples exhibited characteristics that could affect the radionuclide Kd results. These characteristics are summarized in Table 20.

The rock samples that contained sulfides and/or ferrous (Fe^{2+}) iron and manganous (Mn^{2+}) manganese have the potential for changing the oxidation states of antimony, neptunium, plutonium, ruthenium, technetium and uranium (Ames and Rai, 1978). They tend to buffer the equilibration system redox potential at a relatively low value. Any contaminating metallic iron in the rock sample due to sizing operations also will exert the same Eh buffering tendency. Hence, the radionuclide Kd value may remain constant during the equilibration until the buffering systems have been oxidized, and then begin to drift.

The relatively water-soluble mineral phases in the rock samples include calcite, dolomite, gypsum, anhydrite and magnesite. These minerals act to affect Kd values by contributing additional competing cations to the equilibrating solution, including more nonradioactive strontium, for example, than would normally be present as radioactive strontium. With the rock samples containing these water-soluble phases, the nonradioactive solution has to contain sufficient common ions to prevent dissolution, or the nonradioactive solution has to be preequilibrated before adding the radionuclide. In the latter case, the solution should be analyzed to determine its final composition at equilibrium.

The carbonates contained in the rock samples, including calcite, dolomite and siderite, change the equilibrating solution pH and chemical composition.

The apatites, garnets, allanites and zircons all have the potential for containing rare earths, uranium and thorium. These minerals are generally very sparingly water soluble at near-neutral pH, but become of concern at low or high equilibrating solution pH values as sources of uranium, thorium and rare earths.

TABLE 20. Summary of Rock Characteristics that Could Affect Radionuclide Kd Results at Room Temperature

	CONTAINED SULFIDES	CONTAINED FERROUS IRON OR MANGANOUS MANGANESE	CONTAINED WATER-SOLUBLE MINERAL PHASES	CONTAINED PH-BUFFERING CARBONATES	CONTAINED APATITES, ALLANITES OR ZIRCONS	CONTAINED GLASS
WESTERLY GRANITE	•	•	•	•	•	
ARGILLACEOUS SHALE	•	•	•	•	•	
OOLITIC LIMESTONE	•		•	•		
SENTINEL GAP BASALT		•				•
CONASAUGA SHALE	•	•	•	•	•	
CLIMAX GRANITE		•			•	
ANHYDRITE			•			
MAGENTA DOLOMITE			•	•		
CULEBRA DOLOMITE			•	•		

The Sentinel Gap Basalt, as an extrusive rock, contains a glassy groundmass due to relatively rapid cooling. The amount of glass in the rock is a function of where the sample came from in the flow. Toward flow surfaces, the glass content can be very high, with almost no glass in the center of the flow due to slower cooling. At temperatures of 100 to 300 C, the thermodynamically unstable glass reacts rapidly with aqueous solutions yielding more stable, crystalline phases such as quartz and microcline. At lower temperatures, the reaction rates are much slower, but nevertheless much faster than that of the crystalline phases in the basalt. It is suggested that the final chemical composition of the equilibrating solution be determined when the rock sample used is basalt or a relatively soluble rock such as anhydrite, dolomite or limestone.

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