U.S. DEPARTMENT OF THE INTERIOR

U. S. GEOLOGICAL SURVEY

Method descriptions and bibliography of routine work performed by the Branch of Geochemistry analytical laboratories, U.S. Geological Survey.

by

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and

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1. Introduction.

The REPORT program described in part A of this document can be used by *any* analytical laboratory to prepare reports for submitters of samples. In this section, we reproduce the output of the REPORT program for all of the standard methods used *only* in the Branch of Geochemistry at the USGS. Thus, the information that follows serves a dual purpose: it demonstrates how output from the REPORT program looks (or should look, for those attempting to install the program for the first time), and it documents current analytical methods at the USGS.

Method descriptions that appear below are based on information that appears in a) USGS Open File Report 90-688, "Quality assurance manual for the Branch of Geochemistry," B.F. Arbogast, editor; b) USGS Bulletin 1770, "Methods for Geochemical analysis," P.A. Baedecker, editor; c) literature cited in these two publications; and, d) unpublished procedures designed by the authors.

2. Sample output.

The sample output that follows was created on an HP LasetJet IIIp printer using the REPORT program. No editing was done to customize the output for any particular job. No elements were added or deleted during processing, so the output reflects the range of elements that can be determined on a routine basis by each method. Note that the bibliography at the end of the sample output contains *all* cited references, merged and alphabetized, with duplicates removed; this is a standard feature of the REPORT program.

United States Department of the Interior
GEOLOGICAL SURVEY

Branch of Geochemistry, Reston, Virginia

Summary of Analytical Methods for **CG01**

Submitted by *Jon Q. Submitter*

The following paragraphs are brief descriptions of the procedures used by the Branch of Geochemistry to analyze samples in job CG01 *only*. For the work done in Reston, the report has been examined by the chemist who supervises that method; any changes to the standard operating procedure or specific observations about these samples are noted. Paragraphs that describe work done in other USGS centers describe the last known standard procedure. Descriptions of analytical procedures include up-to-date literature citations covering the details of the methods which would be beyond the scope of the "Methods" section in a typical geochemistry manuscript. Abbreviations used below may include: atomic absorption spectrometry (AA), flame atomic absorption spectrometry (FAA), graphite furnace atomic absorption spectrometry (GFAA), inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), instrumental neutron activation analysis (INAA), and X-ray fluorescence spectrometry (XRF).

Sample Preparation: Grinding (L.J. Winters, analyst)

Large rock fragments (>5 cm) are crushed to ~8 mesh (2 to 3 mm) in a jaw crusher with adjustable, hardened Mn-steel plates. The entire sample is run through a "vertical" grinder with alumina plates, producing a powder of ~100 mesh (i.e., most particles are <150 μm). If finer grinding was requested, the sample is reprocessed in an automatic grinder consisting of an agate puck that rotates inside an agate ring, producing a powder of ~200 mesh (<75 μm). Grinding equipment is cleaned before each sample by processing quartz-sand. [Analyses done at Reston center.]

Sample Preparation: Splitting (N.S. Alsop, analyst)

If a sample must be divided into subsamples for use in different laboratories, the powder is thoroughly mixed, poured onto glassine paper, and divided into four piles. Small portions are taken from throughout each mound with a spatula, and placed in a new bottle. For large samples, cone splitters or riffle splitters may be used to obtain subsamples. [Analyses done at Reston center.]

ICP Multielement Analysis (A.F. Dorrzapf, analyst)

A 100-mg sample is decomposed with HNO_3, $HClO_4$, and HF and evaporated to dryness overnight. The residue is dissolved in 10 mL of 2N HCl. Analysis of Ba, Be, Ce, Cr, Cu, Li, Ni, Sc, Sr, V, Y, Zn, Al, Ca, Fe, K, Mg, Mn, Na, P and Ti is done directly on this solution by ICP-AES (Lichte *et al.*, 1987). Dilutions may be required for higher concentrations of major elements. If the samples are low (<10 ppm) in Co, Cr, Cu and

V the solutions are analyzed directly by GFAA (Aruscavage and Crock, 1987). Ni at <20 ppm is analyzed by GFAA using a magnesium nitrate matrix modifier. Note: the presence of the minerals barite, chromite or ilmenite in samples may result in low results for Ba, Cr and Ti, respectively. [Analyses done at Reston center.]

Atomic Absorption Spectrometry Analysis (P.J. Aruscavage, analyst)

A 100-mg sample is decomposed with HNO_3, $HClO_4$, and HF and evaporated to dryness overnight. The residue is dissolved in 10 mL of 2N HCl. Analysis of Co, Cu, Li, Ni, Pb and Zn is done directly on this solution by FAA (Aruscavage and Crock, 1987). If the samples are low (<10 ppm) in Co, Cr, Cu and V the solutions are analyzed directly by GFAA (Aruscavage and Crock, 1987). Ni at <20 ppm is analyzed by GFAA using a magnesium nitrate matrix modifier. Analysis of Cd and Pb (<20 ppm) is done by GFAA using an ammonium phosphate matrix modifier. [Analyses done at Reston center.]

Analysis of As and Sn by Chemical separation/GFAA (M.W. Doughten, analyst)

A 50-mg sample is fused with NaOH. The fusion cake is dissolved in 5 mL water, and 10 mL of 9M H_2SO_4 is added. NaI is added, and the iodide form of As and Sn is extracted into toluene. Analysis is done by GFAA using the arsenic procedure for coal developed by Aruscavage (1977). Primary standard solutions are taken through the procedure along with the samples. Note: this method is known to give low results for sulfide-rich, cassiterite-rich and especially niccolite-rich (NiAs) samples. [Analyses done at Reston center.]

Analysis of Sb by Chemical Separation/GFAA (W.M. d'Angelo, analyst)

A 100-mg sample is decomposed using HNO_3, HF, and H_2SO_4 and evaporated to dryness overnight. 10 mL of H_2O is then added to the sample. NaI is added, and Sb is extracted into toluene as the iodide. Analysis is done by GFAA using the procedure for coal of Aruscavage (1977). Primary standard solutions are taken through the procedure along with the samples. Note: the presence of major amounts of sulfides can cause interferences. [Analyses done at Reston center.]

Analysis of Bi by Chemical separation/GFAA (C.J. Skeen, analyst)

A 100-mg sample is decomposed using HF and $HClO_4$ and evaporated to dryness overnight. 10 mL of H_2O and 2 mL of $HClO_4$ are added to dissolve the residue. Ascorbic acid is added to convert the Bi to a form that is extractable as the iodide (with the addition of NaI) into butyl acetate. The organic layer is analyzed by GFAA. Primary standard solutions are taken through the procedure along with the samples (method of Terashima, 1984). [Analyses done at Reston center.]

Analysis of Se by Chemical Separation/GFAA (P.J. Aruscavage, analyst)

A 100-mg sample is decomposed using HNO_3, $HClO_4$, and HF and evaporated to dryness overnight. The residue is dissolved in 1N HBr. Ascorbic acid is added to convert the Se to a form that is extractable into butyl acetate. 1 mL of the organic layer is evaporated to dryness. 1 mL of HNO_3 and 10 μL of a 1% Fe solution are added; the acid decomposes the organic residue, and the Fe prevents volatilization of Se. The remaining residue is dissolved in 1 mL of 5% HNO_3, and the solution is analyzed by GFAA. Primary standard solutions are taken through the procedure along with the samples. [Analyses done at Reston center.]

Analysis of Silver by Chemical Separation/GFAA (N. Rait, analyst)

Following the method of Aruscavage and Campbell (1979), a 200-mg sample is decomposed using HNO_3, $HClO_4$, and HF, and evaporated to dryness overnight. The residue is dissolved in 15 mL of 20% tartaric acid. The Ag is extracted into butyl acetate as the diphenylthiourea complex. The organic layer is analyzed for Ag by GFAA. Standard solutions are taken through the procedure along with the samples. [Analyses done at Reston center.]

Analysis of Tl by Chemical Separation/GFAA (C.J. Skeen, analyst)

Following the method of Simon *et al.* (1977), 200 mg of sample is decomposed using HNO_3, $HClO_4$, and HF, and is evaporated overnight. The residue is dissolved in 10 mL of 0.5M HCl. Hydroiodic acid is added, and Tl is extracted as the iodide into amyl acetate. The organic layer is analyzed by GFAA. Primary standard solutions are taken throught the procedure along with the samples. [Analyses done at Reston center.]

Analysis of Ge by Chemical Separation/GFAA (M.W. Doughten, analyst)

Following the method of Schnepfe (1979), a 100-mg sample is decomposed using HNO_3, $HClO_4$, HF, and H_2SO_4. The Ge is extracted into toluene and then back-extracted into a 5% HNO_3—1000 ppm Ni solution. This solution is analyzed for Ge by GFAA. Primary standard solutions are taken through the procedure along with the samples. [Analyses done at Reston center.]

Analysis of Au by Chemical Separation/GFAA (J.R. Gillison, analyst)

A 10-g sample is heated in a furnace at 700°C to remove sulfides. The sample is then decomposed with HBr and Br_2. Gold is extracted into MIBK. The organic layer is analyzed for Au by GFAA (Meier, 1980). Primary standards are taken through the extraction procedure along with the samples. [Analyses done at Reston center.]

Analysis of Hg by Cold Vapor AA (J.R. Gillison, analyst)

A 100-mg sample is decomposed using HNO_3 and $HClO_4$ for 2 hours, and diluted with 25 mL of H_2O and 1 mL of HNO_3. This solution is analyzed for Hg by cold vapor AA using the method of Flanagan *et al.* (1982). Primary standard solutions are analyzed with the samples. [Analyses done at Reston center.]

Analysis of Mo, Nb and W by Ion Exchange Separation/ICP-AES (M.W. Doughten, analyst)

A 100-mg sample is decomposed with HNO_3, $HClO_4$, and HF and evaporated to dryness overnight. The residue is dissolved in 15 mL of 8N HCl. The solution is passed through an ion exchange column to remove the alkali metals. The chloride form of Mo, Nb and W is adsorbed onto the resin. The column is washed with 5N HF to remove Fe. A solution of 7N HNO_3 is poured through the column to quantitatively strip the Mo, Nb and W from the resin. This fraction is collected and evaporated to dryness. The residue is dissolved in 2 mL of 2N HCl and analyzed by ICP-AES. Estimates of detection limits are given by Wilson *et al.* (1987). [Analyses done at Reston center.]

Analysis of Te by Ion Exchange Separation/GFAA (M.W. Doughten, analyst)

A 200-mg sample is decomposed using HNO_3, $HClO_4$, and HF and evaporated to dryness overnight. The residue is dissolved in 10N HCl. This solution is passed through an ion exchange column. The chloride form of Te is adsorbed onto the resin. The column is washed with 5N HF to remove Fe. A solution of 7N HNO_3 is poured through the column to strip the Te from the resin. This fraction is collected and evaporated to dryness overnight. The residue is dissolved in 1 mL of a 5% HNO_3—5% HF solution. This solution is analyzed for Te by GFAA. Primary standard solutions are added as a spike to USGS standard rock G-2 and taken through the procedure along with the samples. Note: Very high Zn will interfere with Te analysis. [Analyses done at Reston center.]

Analysis of F and Cl Anions by Ion Chromatography (W.M. d'Angelo, analyst)

Analysis of fluorine is done by the method of Wilson and Gent (1982). Analysis of chlorine is done by the methods of Wilson (1983). A 100-mg sample is fused with Na_2CO_3. The fusion cake is dissolved in H_2O and diluted to 50 mL. A 0.1-mL aliquot is injected into the ion chromatograph, the anions are separated and measured by a conductivity detector. Primary standards are used to calibrate the instrument. [Analyses done at Reston center.]

Analysis of Anions in Aqueous Samples (W.M. d'Angelo, analyst)

Starting with at least 3 mL of aqueous sample, F, Cl, Br, NO_3, NO_2, PO_4 and SO_4 are measured on the ion chromatograph. Samples are filtered before they are injected into the apparatus. [Analyses done at Reston center.]

Analysis of Major Elements by ICP (H. Smith, analyst)

A 100-mg sample is fused with a lithium metaborate/tetraborate flux, and dissolved in 200 mL of dilute HNO_3. Indium is used as an internal standard (1 ppm). The solution is analyzed for major elements by ICP (Jackson *et al.*, 1987), usually in conjunction with the X-ray support package. [Analyses done at Reston center.]

Analysis of Major Element Oxides by "Rapid Rock" (J.R. Gillison, analyst)

Following the method of Shapiro *et al.* (1975), 200 mg of samples are fused with a lithium meta-borate/tetra-borate flux. The fused sample is dissolved in dilute HNO_3. Silicon, Al, P, and Ti are determined colorimetrically. Total Fe, Ca, K, Mg, Mn, and Na are determined by FAA. If FeO was determined by the X-ray Support package, Fe_2O_3 is calculated by difference from total Fe and FeO. All elements are reported as oxides. [Analyses done at Reston center.]

"X-Ray Support" Package for FeO, CO_2, H_2O^+, and H_2O^- (C.L. Prosser, analyst)

FeO (Peck, 1964): A 500-mg sample is decomposed using HF and H_2SO_4. This solution is treated with boric, sulfuric, and phosphoric acids. Fe (II) is determined by a colorimetric titration with potassium dichromate. Sodium diphenylamine sulfonate is used as the endpoint indicator.

CO_2 (Engleman *et al.*, 1985): A 500-mg sample is digested with $HClO_4$. CO_2 is evolved and carried into a coulometric cell. The CO_2 is converted into a strong acid by ethanolamine and is titrated coulometrically.

H_2O^- (Shapiro, 1975): A 1-g sample is weighed and dried at 110°C for a minimum of 1 hr. After cooling in a dessicator, the sample is weighed again and H_2O^- is calculated by difference.

H_2O^+ (Jackson *et al.*, 1987): A 50-mg sample is mixed with 150 mg of lead oxide/lead chromate flux. The sample is heated to 950°C. The evolved water is determined coulometrically by Karl-Fischer titration. This gives the total H_2O in the sample. H_2O^+ is determined from the difference between total H_2O and H_2O^-. [Analyses done at Reston center.]

"X-Ray Support" Package for FeO (J.W. Marinenko, analyst) FeO (Peck, 1964): A 500-mg sample is decomposed using HF and H_2SO_4. This solution is treated with a solution of boric, sulfuric, and phosphoric acids. Fe (II) is determined by a colorimetric titration with potassium dichromate. Sodium diphenylamine sulfonate is used as the endpoint indicator. [Analyses done at Reston center.]

Analysis of Cl by Selective Ion Electrode (C.J. Skeen, analyst)

A 200-mg sample is decomposed using HF, H_2SO_4, and $KMnO_4$ in a specially designed, sealed teflon container. Chlorine is captured in a KOH/Na_2SO_3 solution in a center compartment of the container. Chlorine is determined as chloride by the selective ion electrode (SIE) method of Aruscavage and Campbell (1983). [Analyses done at Reston center.]

Analysis of F by Selective Ion Electrode (J.R. Gillison, analyst)

A 100-mg sample is fused with a Na_2CO_3/ZnO flux. The fusion cake is leached with H_2O. HCl is added to expel CO_2. An aliquot of the sample solution is buffered with a sodium citrate/KNO_3 solution. This solution is analyzed for fluorine, as fluoride, by the selective ion electrode (SIE) method of Kirschenbaum (1988). [Analyses done at Reston center.]

Analysis of F by Selective Ion Electrode (J.R. Gillison, analyst)

A 100-mg sample is fused with a Na_2CO_3/ZnO flux. The fusion cake is leached with H_2O. HCl is added to expel CO_2. An aliquot of the sample solution is buffered with a sodium citrate/KNO_3 solution. This solution is analyzed for fluorine, as fluoride, by the selective ion electrode (SIE) method of Kirschenbaum (1988). [Analyses done at Reston center.]

Analysis of S by Combustion/IR Spectroscopy (H. Smith, analyst)

A 200-mg sample is weighed. Vanadium pentoxide is added as a combustion aid. The sample is combusted in a sulfur analyzer and the sulfur dioxide evolved is measured by an IR detector (Kirschenbaum, 1983). [Analyses done at Reston center.]

Analysis of Carbon, Hydrogen, and Nitrogen (C.J. Skeen, analyst)

A 1- to 20-mg sample (depending on concentration and/or sample type) is combusted in a CHN elemental analyzer. C, H, and N are converted to CO_2, H_2O, and N_2 and separated by chromatography. Concentrations of these gases are determined by a thermal conductivity detector. Acetanilide is used as the calibration standard. [Analyses done at Reston center.]

Analysis of Platinum Group Elements by Fire Assay/GFAA (H. Smith, analyst)

A 15-gram sample and 2 mg of gold wire are fused with a PbO/Na_2O_3/Borax-glass/flour flux for 45 min. at 1000°C. The lead button is separated from the fusion slag. Bone-ash cupels are preheated at 1000°C, and the lead buttons are added. After the buttons have melted the temperature is reduced to 850°C and air is passed over the cupels. The lead is oxidized to PbO and is absorbed into the bone ash, leaving a gold bead which is dissolved in aqua regia and evaporated to dryness. The residue is taken up in 6M HCl, and analyzed for Pd, Pt and Rh by GFAA (Aruscavage *et al.*, 1984). [Analyses done at Reston center.]

Analysis of Cr, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Ba, La and Ce by Energy-Dispersive XRF (J.R. Evans and G.A. Sellers, analysts)

Approximately 1.0 g of 100-mesh, powdered sample is pressed into a Mylar cup. Samples are analyzed for Cr, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Ba, La and Ce using a Kevex 700 EDXRF spectrometer with a Kevex 7000 analyzer (Johnson, 1984; Johnson and King, 1987). The secondary targets used to fluoresce each element were:

Cr : Iron
Ni, Cu and Zn : Germanium
Rb, Sr, Y, Zr and Nb : Silver
Ba, La and Ce : Gadolinium

Corrections are made for background interferences, escape peaks, and spectral overlaps. Sources of error inherent to EDXRF analysis are corrected using the Compton ratio method. Trace element concentrations in the samples are calculated from calibration graphs of the intensity ratio vs. concentration for a series of standard reference materials found in Abbey (1983). [Analyses done at Reston center.]

"Long Count" INAA package (P.A. Baedecker, J.N. Grossman and G.A. Wandless, analysts)

Sample aliquants of ~0.5 g each are irradiated for 6-8 hours at a flux of $\sim 2 \times 10^{12}$ $n\text{-}cm^{-2}\text{-}s^{-1}$ in the "TRIGA" reactor at the U.S. Geological Survey, Denver, CO. Standards for most elements are aliquants of a powdered natural obsidian spiked with primary solutions, taken to dryness and homogenized. Standards for Ca, Ti and Au are powdered $CaCO_3$, TiO_2, and homogeneous low-Au quartz, respectively. At least one replicate sample and one USGS standard rock are irradiated together with the samples and standards.

Samples are counted three times on co-axial Ge and/or Ge(Li) detectors with resolutions ranging from 1.78 to 1.86 KeV measured at 1.33 MeV using the following scheme: 1-hour counts after 6-8 days of decay, 2-hour counts after 14-17 days of decay, and 2-4 hour counts ~50 days after irradiation. In addition, one count is done on an intrinsic Ge, low-energy photon detector (for 1 hour, 8-10 days after irradiation).

Gamma-ray spectra are analyzed for Na, K, Ca, Sc, Ti, Cr, Fe, Co, Ni, Zn, As, Se, Rb, Sr, Zr, Mo, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, Au, Th and U using the isotopes listed on the INAA report cover-sheet. Computer processing is done with SPECTRA and associated programs on a VAX 11/780 computer or an IBM-PC compatible computer (Grossman and Baedecker, 1987; Baedecker and McKown, 1987; Baedecker and Grossman, 1989). Corrections are made for spectral interferences as well as for interferences on Zr, Mo, Ba, La, Ce and Nd from the products of ^{235}U fission produced during irradiation.

Uncertainties listed in the reports reflect 1-σ counting statistics. Upper limits are calculated from the area of a peak 3-σ above the measured background. [Analyses done at Reston center.]

"Short Count" INAA Package (C.A. Palmer and M.J. Pickering, analysts)

Sample aliquants of ~0.5 g each are irradiated for 6-8 hours at a flux of $\sim 2\times10^{12}$ n-cm^{-2}-s^{-1} in the "TRIGA" reactor at the U.S. Geological Survey, Denver, CO. Standards for most elements are aliquants of a powdered natural obsidian spiked with primary solutions, taken to dryness, and homogenized. Standards for Ca, Ti and Au are powdered $CaCO_3$, TiO_2, and homogeneous low-Au quartz, respectively. At least one replicate sample and one USGS standard rock are irradiated together with the samples and standards.

Samples are counted two times on co-axial Ge and/or Ge(Li) detectors with resolutions ranging from 1.78 to 1.86 KeV measured at 1.33 MeV using the following scheme: 1-hour counts after 6-10 days of decay, and 2-hour counts after 14-17 days of decay.

Gamma-ray spectra are analyzed for Na, K, Ca, Sc, Ti, Cr, Fe, Co, Ni, Zn, As, Se, Rb, Sr, Mo, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, Au, Th and U using the isotopes listed on the INAA report cover-sheet. Computer processing is done with SPECTRA and associated programs on a VAX 11/780 computer or an IBM-PC compatible computer (Grossman and Baedecker, 1987; Baedecker and McKown, 1987; Baedecker and Grossman, 1989). Corrections are made for spectral interferences as well as for interferences on Mo, Ba, La, Ce and Nd from the products of ^{235}U fission produced during irradiation.

Uncertainties listed in the reports reflect 1-σ counting statistics. Upper limits are calculated from the area of a peak 3-σ above the measured background. [Analyses done at Reston center.]

Analysis of Platinum Group Elements by ICP-MS (G.O. Riddle, analyst)

A 10-g sample is fused with a $Ni/S/SiO_2/Na_3CO_2$/borax-glass flux for 2 hours at 1050°C. The resulting NiS button is removed, broken into pieces, and placed into a test tube. 1 mL of 20% $SnCl_2$, 0.1 mL of 1% tellurium solution, and 50-70 mL of concentrated HCl are added to the tube to dissolve the NiS button and coprecipitate the Pt metals with Te. The solution is filtered and the Te(Pt metal) residue is collected on polycarbonate filter paper. The filter paper and precipitate are dissolved in HCl and HNO_3, diluted to 10 mL with 1% HCl and the solution is analyzed for Pd, Pt, Rh, Ru and Ir by ICP-MS. [Analyses done at Denver center.]

"X-Ray Support" Package for FeO, CO_2, H_2O^+, and H_2O^- (C. Papp, analyst)

FeO (Peck, 1964): A 500-mg sample is decomposed using HF and H_2SO_4. This solution is treated with boric, sulfuric, and phosphoric acids. Fe (II) is determined by a potentiometric titration with potassium dichromate.

CO_2 (Engleman *et al.*, 1985): A 500-mg sample is digested with $HClO_4$. CO_2 is evolved and carried into a coulometric cell. The CO_2 is converted into a strong acid by ethanolamine, and titrated coulometrically. H_2O^- (Shapiro, 1975): A 1-g sample is weighed and dried at 110°C for a minimum of 1 hr. After cooling in a dessicator, the sample is weighed again and H_2O^- is calculated by difference.

H_2O^+ (Jackson *et al.*, 1987): A 50-mg sample is mixed with 150 mg of lead oxide/lead chromate flux. The sample is heated to 950°C. The evolved water is determined coulometrically by Karl-Fischer titration. This gives the total H_2O in the sample. H_2O^+ is determined from the difference between total H_2O and H_2O^-. [Analyses done at Denver center.]

Analysis of Carbon by Combustion/IR spectroscopy (L. Filipek, analyst)

0.25 to 1.00 g of sample is combusted in a carbon analyzer. The evolved carbon dioxide is measured by an IR detector (Jackson *et al.*, 1987). [Analyses done at Denver center.]

Analysis of Sulfur by Combustion/IR spectroscopy (D. Detra, analyst)

A 250-mg sample is weighed and combusted in a sulfur analyzer with vanadium pentoxide. The evolved sulfur dioxide is measured with an IR detector (Kirschenbaum, 1983). [Analyses done at Denver center.]

Analysis of Cl by Selective Ion Electrode (R. Leinz, analyst)

A 200-mg sample is decomposed using HF, H_2SO_4, and $KMnO_4$ in a specially designed, sealed teflon container. Chlorine is captured in a KOH/Na_2SO_3 solution in a center compartment of the container. Chlorine is determined as chloride by the selective ion electrode (SIE) method of Aruscavage and Campbell (1983). [Analyses done at Denver center.]

Analysis of F by Selective Ion Electrode (L. Gough, analyst)

A 50-mg sample is fused with a $Na_2CO_3/K_2CO_3/KNO_3$ flux in a Pyropot heating block for 10 min. 15 mL of 1M citric acid is added to the cooled sample, and the solution is transfered to a beaker containing a sodium citrate buffer. The volume is adjusted to 100 mL, and the fluoride concentration is determined by selective ion electrode potentiometry (Hopkins, 1977; O'Leary and Meier, 1986) [Analyses done at Denver center.]

ICP Multielement Package (P.H. Briggs, analyst)

Major and trace elements are determined in geologic materials by ICP-AES using the method of Lichte *et al.* (1987) and Crock *et al.* (1983). The sample is decomposed using a mixture of hydrochloric, nitric, perchloric, and hydrofluoric acid at low temperature. Lutetium is added as an internal standard. The digested sample is taken to dryness, the residue treated with aqua regia, and the solution brought to 10 grams with dilute nitric acid. The solution is nebulized into the ICP-AES plasma discharge for determination of the Ag, Al, As, Au, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Eu, Fe, Ga, Ho, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Sc, Sn, Sr, Ta, Th, Ti, U, V, Y, Yb and Zn . [Analyses done at Denver center.]

Analysis of Ag, As, Au, Bi, Cd, Cu, Mo, Pb, Sb and Zn by Solvent Extraction ICP-AES (J.M. Motooka, analyst)

A 1.0-g sample is treated with HCl and H_2O_2. The solution is placed in a boiling water bath for 20 min. After cooling, an ascorbic acid/potassium iodide solution is added. Diisobutylketone containing a tertiary amine hydrochloride (Aliquat 336) is added, and the sample is shaken. The sample is centrifuged, and the organic phase is analyzed for Ag, As, Au, Bi, Cd, Cu, Mo, Pb, Sb and Zn by ICP-AES (Motooka, 1988). [Analyses done at Denver center.]

Analysis of Water-extractable Boron by ICP-AES (D.L. Fey, analyst)

A 5.0-g sample is combined with 10 g of deionized water and heated in a boiling water bath for 1 hour. The sample is cooled and centrifuged. 3 mL of the solution is transferred to a test tube containing 2 drops of HNO_3 and 30 μL of a solution containing 500 ppm lutetium. The sample is analyzed for B by ICP-AES using Lu as an internal standard. [Analyses done at Denver center.]

Multielement Analysis by DC-Arc Emission Spectrography. (T. Hopkins, analyst)

A 10-mg sample is weighed and mixed with 20 mg of pure graphite. The sample is packed into the cavity of a graphite electrode. The sample is burned to completion in a direct-current arc at 12-15 amperes. The spectrum of the sample is recorded on photographic film and concentrations of the elements are determined by visual comparison with the spectra of standards (method of Grimes, 1968, and Myers *et al.*, 1961). [Analyses done at Denver center.]

Analysis of As, Sb and Se by Hydride Generation AA. (R. O'Leary, analyst)

A 0.30-g of sample is digested with $K_2S_2O_8$, HF, HNO_3, and $HClO_4$ followed by additional treatment with HNO_3, $HClO_4$, and H_2SO_4. H_2O and HCl are added and further heating applied. The solution is diluted to 34 g total weight with H_2O. The sample solution is mixed with sodium borohydride, and the resulting metal hydride is passed in an argon stream into a heated quartz tube The metal concentration is measured by atomic absorption spectroscopy (Crock and Lichte, 1982; Briggs and Crock, 1986). [Analyses done at Denver center.]

Analysis of Au by Chemical Separation/GFAA (J.G. Crock, analyst)

A 10-g sample is heated in a furnace at 700°C to remove sulfides. The sample is then decomposed with HBr and Br_2. Gold is extracted into MIBK. The organic layer is analyzed for Au by GFAA (Meier, 1980). Primary standards are taken through the extraction procedure along with the samples. [Analyses done at Denver center.]

Analysis of Au, Te and Tl by Chemical Separation/FAA (E. Welsch, analyst)

A 4.0-g sample is decomposed with HF, HCl, and HNO_3 and taken to dryness. HBr is added and the sample is again dried. The residue is dissolved in a dilute HBr-Br_2 mixture and diluted to 20 mL. Au and Tl are extracted into methyl-isobnutyl ketone (MIBK) and determined by FAA. The MIBK layer is discarded and concentrated HBr is added. Ascorbic acid is added to reduce Fe, and Te is extracted into MIBK and determined by FAA (Hubert and Chao, 1985). [Analyses done at Denver center.]

Analysis of Hg by Cold Vapor AA (Unknown Analyst)

A 0.1-g sample is digested in a closed vessel with HNO_3 and $Na_2Cr_2O_7$. A hydroxylamine hydrochloride-sodium chloride/H_2SO_4 solution is added to the sample. Hg(II) is reduced with stannous chloride. Mercury is transported by an airstream to an optical absorption cell and measured by atomic absorption spectroscopy (Wilson *et al.*, 1987). [Analyses done at Denver center.]

Analysis of U by UV-Fluorescence (D. Smith, analyst)

A 0.5-g sample is digested with HNO_3 and taken to dryness. The residue is treated with dilute HNO_3 and boiled for 5 min. An $Al_2(NO_3)_3$ solution is then added. The solution is cooled and ethyl acetate is added. The sample is shaken for 2 min. and then centrifuged. A 5-mL aliquot of the ethyl acetate layer is transferred to a platinum crucible and ignited. 2 g of Na_2CO3/K_2CO3 flux is added and the sample is fused. Uranium is measured in the wafer using an ultraviolet fluorimeter (O'Leary and Meier, 1986). [Analyses done at Denver center.]

Analysis of W by UV-Vis spectrophotometry. (E. Welsch, analyst)

A 1.0-g sample is digested with HF and HNO_3. The residue is dissolved in 80% HCl. The solution is centrifuged and a 5-mL aliquot is transferred to another test tube. 5 mL of a $SnCl_2$/HCl solution is added and the sample is heated. A zinc dithiol in etanol solution is added to complex tungsten. The complex is extracted into heptane, and the organic layer is analyzed for W with a UV-VIS spectrophotometer (Welsch, 1983). [Analyses done at Denver center.]

Analysis of Major Elements by XRF (J.S. Mee, D.F. Siems and J.E. Taggart, analysts)

Ten major elements are determined in rocks and minerals by wavelength dispersive X-ray fluorescence spectrometry (WDXRF) (Taggart *et al.*, 1987). 800-mg samples are weighed and then ignited in a Pt-Au crucible at 925°C for 45 minutes. After cooling, the samples are reweighed to determine the total loss on ignition (LOI). The ignited samples are fused with 8 g of lithium tetraborate by heating at 1120°C for 40 minutes, poured into molds, and the resultant glass discs are irradiated by X-rays generated by a Rh-target tube operating at 35-kV and a current of 60 mA. Characteristic X-rays emitted by each element are counted, corrected for matrix effects using the deJongh (1973) model, and concentrations are determined using previously prepared calibration standards. Concentration data are then recalculated to account for any mass change on ignition. [Analyses done at Denver center.]

"X-Ray Support" Package for FeO, CO_2, H_2O^+, and H_2O^- (Unknown Analyst)

<u>FeO</u> (Peck, 1964, Cramer *et al.*, 1984): A 500-mg sample is decomposed using HF and H_2SO_4. This solution is treated with boric, sulfuric, and phosphoric acids. Fe (II)

is determined by an automated colorimetric titration with potassium dichromate using sodium diphenylamine sulfonate as an indicator.

$\underline{CO_2}$ (Engleman *et al.*, 1985): A 500-mg sample is digested with $HClO_4$. CO_2 is evolved and carried into a coulometric cell. The CO_2 is converted into a strong acid by ethanolamine, and titrated coulometrically.

$\underline{H_2O^-}$ (Shapiro, 1975): A 1-g sample is weighed and dried at 110°C for a minimum of 1 hr. After cooling in a dessicator, the sample is weighed again and H_2O^- is calculated by difference.

$\underline{H_2O^+}$ (Jackson *et al.*, 1987): A 50-mg sample is mixed with 150 mg of lead oxide/lead chromate flux. The sample is heated to 950°C. The evolved water is determined coulometrically by Karl-Fischer titration. This gives the total H_2O in the sample. H_2O^+ is determined from the difference between total H_2O and H_2O^-. [Analyses done at Menlo Park center.]

Analysis of F by Selective Ion Electrode (T.L. Fries, analyst)

A 0.08-g sample is fused with lithium metaborate, and the fusion cake is dissolved in dilute nitric acid. A complexing agent and buffer (1,2-diaminocyclohexene-N,N,N,'N'-tetraacetic acid (DCTA) and sodium citrate) are added. Fluoride is determined by selective ion-electrode potentiometry (Bodkin, 1977). [Analyses done at Menlo Park center.]

Analysis of Na_2 and K_2O by Flame Photometry (T.L. Fries, analyst)

A 0.100-g sample is fused with lithium metaborate, and the fusion cake is dissolved with nitric acid. The solution is analyzed simultaneously for sodium and potassium by flame emission spectrometry. Lithium is used as an internal standard (Jackson *et al.*, 1987). [Analyses done at Menlo Park center.]

Analysis of Boron by Emission Spectrography (P.J. Lamothe, analyst)

10 mg of powdered sample is thoroughly mixed and ground with 40 mg of copper hydroxyfluoride (CuOHF) in an agate mortar. Boron is measured on an emission spectrograph using the method of Golightly *et al.* (1987), based on the volatilization of boron fluorides into a direct-current arc. The CuOHF inhibits the formation of refractory boron carbide on the graphite electrode. The concentration of boron, which may range from 0.2 to 600 ppm, is calculated from the intensity of the light emitted from the arc of the sample electrode relative to that of artificial and natural standards run under similar spectrographic conditions. [Analyses done at Menlo Park center.]

Analysis of Cr, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Ba, La and Ce by Energy-Dispersive XRF (J. Kent and B.-S. King, analysts)

Approximately 1.0 g of 100-mesh, powdered sample is pressed into a Mylar cup. Samples are analyzed for Cr, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Ba, La and Ce using a Kevex 700 EDXRF spectrometer with a Kevex 7000 analyzer (Johnson, 1984; Johnson and King, 1987). The secondary targets used to fluoresce each element were:

Cr : Iron
Ni, Cu and Zn : Germanium
Rb, Sr, Y, Zr and Nb : Silver
Ba, La and Ce : Gadolinium

Corrections are made for background interferences, escape peaks, and spectral overlaps. Sources of error inherent to EDXRF analysis are corrected using the Compton ratio method. Trace element concentrations in the samples are calculated from calibration graphs of the intensity ratio vs. concentration for a series of standard reference materials found in Abbey (1983). [Analyses done at Menlo Park center.]

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