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RECONNAISSANCE GEOCHEMISTRY OF SOME ROCKS OF THE GUANAJUATO MINERAL DISTRICT, MEXICO

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RESUMEN

Se usó el análisis instrumental de activación por neutrones para determinar la concentración de unos 16 elementos (Na, K, Rb, Cs, Ba, Th, Fe, Sc, Co, Cr, La, Eu, Zr, Hf, Ta and Sb) en rocas del Distrito Minero de Guanajuato, México. El análisis de las rocas de referencia de la U.S.G.S. muestra que el método es bastante confiable para estudiar la geoquímica de las formaciones de las rocas. Se discuten estos resultados en base a la geología y se señalan sus significados sobre las relaciones petrogenéticas.



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ABSTRACT

Instrumental neutron activation analysis has been used to determine the concentration of some 16 elements (Na, K, Rb, Cs, Ba, Th, Fe, Sc, Co, Cr, La, Eu, Zr, Hf, Ta and Sb) in rocks of the Guanajuato Mineral District, Mexico. Analysis of U.S.G.S. standard rocks shows that the method is quite reliable to study the geochemistry of rock formations. These results are discussed in the light of the known geology and their bearing on the petrogenetic relationships has been pointed out.

INTRODUCTION

The present work is an effort to determine by neutron activation, the concentration of various elements in U.S.G.S. international geochemical reference samples, compare the results with the existing published analyses on these rocks by several other laboratories to show that the method can be applied to obtain reasonably accurate data and extend the method to study the geochemistry of some Mexican rock formations. A reconnaissance study of the Guanajuato Mineral District was therefore undertaken to delineate the geochemistry of this economically important region of Mexico.

GEOLOGY OF THE REGIONS STUDIED

A general location map and the area sampled are given in Figure 1.

A. GUANAJUATO REGION

Geology of this area has been described in Guiza et al (1949) and more recently in the photogeologic map of mineral district of Guanajuato, Mexico, published by CRNNR (1963), and in Echagoyen et al (1970).

Below are summarized some of the salient features of its geology.

1) *Sedimentary rocks*

The oldest rocks of this region are black to greenish brown, reddish brown and gray shales (Trl) of marine origin and probably of triassic age.

These are overlain in some places by remnants of white gray calcareous shales and limestones (TRc), depicting a transition to limestone layers which at one time possibly covered the shales. These limestones are in some places metamorphosed to marble, caused by orogenic movements and the effect of intrusive bodies. These rocks are in turn overlain by ochre yellow, grayish red and blackish gray schists.

During tertiary were deposited sandstones and red conglomerate (EOc) in a fairly extensive area. This formation is named the "Conglomerado rojo de Guanajuato" and is formed of rhyolitic, andesitic, basaltic, granitic and dioritic rocks, limestones and shales. These fragments are derived from triassic and cretaceous rocks except the granitic and dioritic rocks, the origin of which has not been possibly established.

The presence of these fragments in a rounded form has also given a name "frijolillo" to this formation. Ferruginous clay of red color mainly due to the presence of ferrous oxides — hematite and turgite, with small amounts of calcite constitutes the cementing material for this formation and a middle eocene to lower oligocene age has been suggested for this formation based on paleontological studies.

One also finds in this area a sandstone formation locally known as Losero formation (Pt1) which consists of mainly fine volcanic ash, somewhat rounded quartz and feldspar grains and a large amount of silicic volcanic material cemented by calcite.

2) *Extrusive igneous rocks*

Resting over the conglomerate and Losero formation, are found rhyolitic tuffs, breccias and flows of red to pink and gray color, called La Bufa rhyolite (Prb). The presence of kaolin in some places indicates a possible alteration caused by hydrothermal solutions. The rhyolitic masses have marked phenocrysts of quartz and feldspar.

- Coal**
- Alluvium
- Ptz**
- Pc**
- Pac**
- Pcb**
- Ppb**
- Pgd**
- PH**
- ECc**
- Red conglomerate**
- Limestone**
- TRc**
- Shale**
- Contact**
- Faults or fractures**
- Faults indicating subsided block**
- Dyke**
- Vans indicating strike direction**

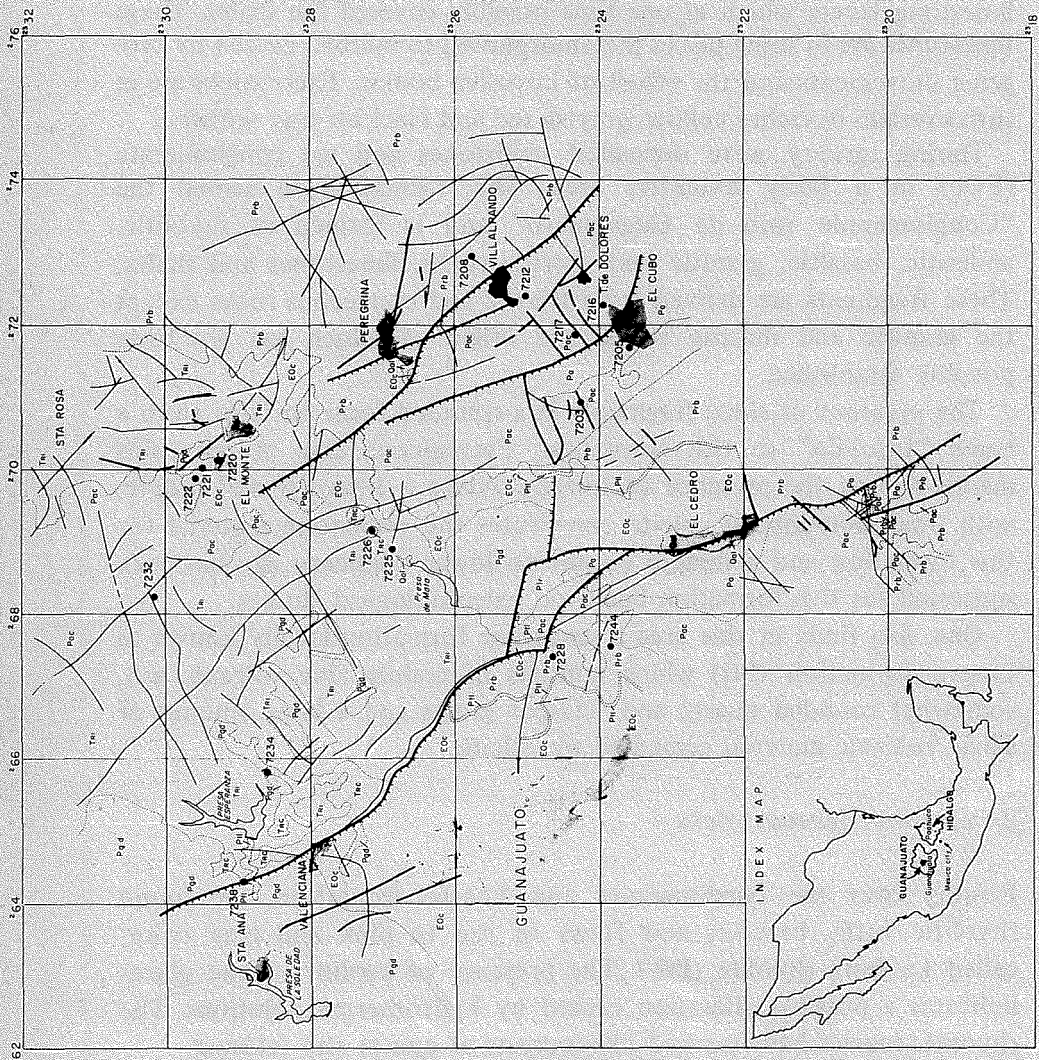
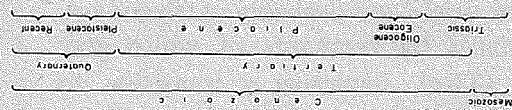


Fig. 1 Geologic map of Guanajuato region indicating sample locations.

Geologic map taken from
C.R.N.R. (1963)

Covering rhyolites, there exists a series of andesitic tuffs (Pac) of mainly green and bluish green color, which has a thickness varying from a few cms to one or more meters. This formation has been given a general name "Calderon" and consists of sandstones, conglomerates, andesitic tuffs and breccias with layering of dacitic tuffs. Several subgroups have been distinguished in this formation.

One then finds El Cedro formation (Pa) of miocene age which consists of andesitic and augite-bearing basaltic bodies having a porphyritic texture and a dark greenish gray to reddish brown color. These rocks are further characterized by phenocrysts of feldspars.

In this area one finds another formation called Chichindaro rhyolite (Plr) which consists of pink colored rhyolitic masses with interstratified layers of breccias and tuffs. A quaternary age has been tentatively assigned to this formation. There also exist recent alluvium deposits (Qal) which are disintegration products of the tertiary and older rocks.

3) Intrusive igneous rocks

Though only one granite diorite intrusion (Pgd) of cream color was distinguished in this area and was placed in age as later to red conglomerate and prior to volcanic rocks and though there existed a number of unclassified intrusives covering diorite, monzonite, and possibly some rhyolitic, andesitic and basaltic intrusive bodies, later work has subdivided the intrusive rocks into several groups depending upon their lithology and relative ages.

One also finds andesitic dykes cutting the volcanic rocks. They are generally vertical and their thickness varies between a few cms and up to 5 meters.

4) Mineral veins

Gold and silver mineralization in this area occurs mainly in fractures and faults having NW-SE direction and is considered to be caused by aqueous solutions having moderate temperatures ($\sim 254^{\circ}\text{C}$). The age

of the mineralization is considered to be somewhat prior to the latest phase of igneous activity represented by volcanic eruptions of acidic lava (Chichindaro rhyolite) towards the end of pliocene.

Based on the results of several workers summarized in Echegoyen et al (1970), the mineral vein samples have native gold and silver, argentite, argyrodite, chalcopyrite, galena, sphalerite, pyrite, marcasite and several others.

B. PACHUCA REGION

The geology of this area has been given in Maldonado (1956a, b) and Geyne et al (1963). Only two samples, both of volcanic rocks, have been analysed from this area in the present study.

A brief summary of the description of the samples studied is given in Table 1.

EXPERIMENTAL DETAILS

Samples of seven U.S.G.S. standard rocks, viz., diabase W-1, granite G-2, granodiorite (adamellite) GSP-1, andesite AGV-1, peridotite PCC-1, dunitite DTS-1 and basalt BCR-1, as well as several other rocks (16 samples from Guanajuato region and 2 from Pachuca region) were taken for this study.

The utility of solid-state Ge (Li) γ -ray detectors in instrumental neutron activation analysis (INAA) has already been realized (e.g., Prussin et al, 1965; Shroeder et al, 1966; Cobb, 1967; Gordon et al, 1968; Brunfelt and Steinnes, 1969).

The method is similar to the one described by Gordon et al (1968). Approximately 800 mgm of each of the pulverized samples were weighed into clean polyethylene vials that were later sealed. Each of the vials was in turn put in small polyethylene bags and sealed. These were then packed in various aluminium cylindrical containers in order to irradiate them in the nuclear reactor at Salazar, Mexico.

Irradiations were carried out for about 40 minutes in the thermal

T A B L E I
A BRIEF DESCRIPTION OF THE SAMPLES ANALYSED

| Sample No. | Our Especification | Description and Locality |
|------------|--------------------|---|
| 7205 | GCCU- Pa- 1- 72 | El Cedro Andesite On the way to El Cubo Village from Guanajuato City, near the entrance of El Cubo. The rock is rather brittle. |
| 7212 | GV- Pac- 4- 72 | Calderon Andesite ~100 meters from Villalpando Village on the way to Tiro Dolores. Road-cutting, but the rock a little weathered. |
| 7216 | GTD- Pac- 4- 72 | Calderon Andesite ~300m. from Tajo de Dolores on the way to Guanajuato. |
| 7228 | GCPM- Prb- 2- 72 | La Bufa Rhyolite On the way to Presa de Mata from Guanajuato, there are Rhyolite outcrops on both sides of the river. |
| 7244 | GCC- Prb- 3- 72 | La Bufa Rhyolite ~1 Km. from Guanajuato on the way to El Cedro Village. |
| 7208 | GV- Prb- 4- 72 | La Bufa Rhyolite ~400 m. beyond Villalpando Village going from Guanajuato. Large outcrops and reddish rock but somewhat weathered. |
| 7221 | GM- Pgd- 1- 72 | Granite-diorite intrusive ~200m. out of El Monte Village collected ~ 10m. above the road. The rock is somewhat weathered. |
| 7222 | GM- EOC- 1- 72 | Red Conglomerate ~300m. from El Monte Village. |
| 7234 | GCSR- TRC- 3- 72 | Limestone ~2 Km. from Guanajuato on the way to Santa Rosa Village and Dolores Hidalgo. Road-cutting. Limestone underlying intrusive rock. Further, it seems that Limestone is somewhat metamorphosed (Contact metamorphism). |
| 7226 | GPM- TRC- 2- 72 | Limestone Coarse-grained rock collected near Presa de Mata on the way to El Monte. The rock somewhat weathered. |

| Sample No. | Our Especification | Description and Locality |
|------------|--------------------|---|
| 7232 | GCSR- TRI - 1 - 72 | Shale On the road from Guanajuato to Santa Rosa Village and Dolo - res Hidalgo. ~2 Km. before arriving Santa Rosa. Fresh road-cutting. |
| 7220 | GM- TRI - 1 - 72 | Shale On the way from Guanajuato to El Monte Village; just entering the village. |
| 7225 | GPM- TRI - 1 - 72 | Shale Fine-grained rock collected near Presa de Mata on the way and ~100m. NE of Shale-Aluvium contact. |
| 7203 | GCCU- Diq - 3 - 72 | Dyke rock Road-cutting on the way from Guanajuato to El Cubo Village. |
| 7217 | GTD- Diq - 1 - 72 | Dyke rock ~800m. from Tajo de Dolores on the way to Guanajuato. Pink-coloured massive rock. |
| 7238 | GCSA- VM- 1 - 72 | Mineral Vein Medium - to - fine grained rock containing shining gold and silver grains. |
| 7101 | QB- 1 - 71 | Basaltic lava ~70 Km. mark on the Mexico-Pachuca highway. Big outcrops of basaltic lava probably of pleistocene age. |
| 7102 | M- 2 - 71 | Chlorite-Andesite On the way from Pachuca to Real del Monte. There exists --- quartzite formation probably of hydrothermal origin. |

column of the reactor at a total flux of about $4 \times 10^{12} \text{ n. cm}^{-2} \text{ sec}^{-1}$ and samples were left to "cool" for a few days before the actual counting was undertaken.

One series of irradiation was carried out for a relatively longer period of about 3 hours, which though resulted in somewhat higher sensitivity for relatively longer-lived species, as expected, made the samples excessively "hot" and a prolonged "cooling" period of several days before counting. However, lesser amounts of samples can be used profitably with longer irradiations.

The vials were taken out of the polyethylene bags and cleaned with acetone and distilled water, before placing them for counting. Several distinct counting intervals were chosen in order to optimize the counting of different species.

DETECTOR AND ELECTRONICS

The Ge (Li) detector used was a 13.8 cm^3 total volume, 9.00 cm^2 active area, 13.7 mm length, and 12.4 cm^3 active volume, trapezoidal detector (Instituto Nacional de Energía Nuclear), which was fed by an Ortec 210 high-voltage supply.

Signals were passed through a Canberra 1408 C, pre-amplifier and a Canberra 1417 spectroscopy amplifier, to a 4096 Channel memory, Hewlett Packard 5401 B multichannel analyzer. Only 1024 channels from the memory were used to register the γ -ray spectra.

Data from the analyzer memory were read out by a Hewlett Packard 5050 B digital printer. The detector was surrounded by a Pb-Shield of approximately 2" thickness in order to reduce the background. The system had an altogether low background; a typical spectrum being shown in Fig. 2.

The spectrum of ^{137}Cs 662-keV γ -rays is shown in Fig. 3. The FWHM of the photopeak is about 4 keV, which is quite good for a detector of this size. The peak-to-Compton ratio is about 7.5.

IDENTIFICATION OF SPECIES

The analyzer system was calibrated with ^{113}Sn (225 and 390 keV), ^{137}Cs (661.6 keV), ^{88}Y (900 and 1840 keV) and ^{60}Co (1173 and 1332 keV) sources for an energy of approximately 2 keV/channel. The calibration was checked everyday. Counting-times used for samples and standards varied between 20 and 250 minutes. The dead time of the system was almost always zero per cent.

Production and properties of various nuclides determinable with purely instrumental neutron activation analysis are shown in Table 2. The identification of species was based largely on the energies of the lines and there was generally very little ambiguity in their assignment.

ABUNDANCE DETERMINATIONS

Because of the unavailability of monitor solutions of different elements, the content of an element in a sample was calculated from the ratio of the peak area in the sample to the area of corresponding peak in a "standard" with presumed content of that element. The areas were corrected for the decay between sample and standard counts, for different counting times, etc.

Some typical spectra are shown in Figs. 4, 5 and 6. It is seen that most of the photopeaks stand out clearly above the general "background" level which is largely due to the Compton scattering of higher γ -rays. Thus there was little difficulty in determining the peak areas. The spectrum over a "window" of 4 or 5 channels (8 to 10 keV) around the maximum was integrated and the "background" determined from the channels on both sides of the window, was subtracted to get the net-peak area. The data reduction could as well be carried out on a digital computer (Inouye et al, 1969).

For cases in which the areas of several peaks originating from a given nuclide could be determined in a spectrum, the ratio of each of the peak areas to the corresponding areas in the standard was computed. The individual ratios were weighed by the counting statistics and combined to give an average ratio of the sample-to-stan-

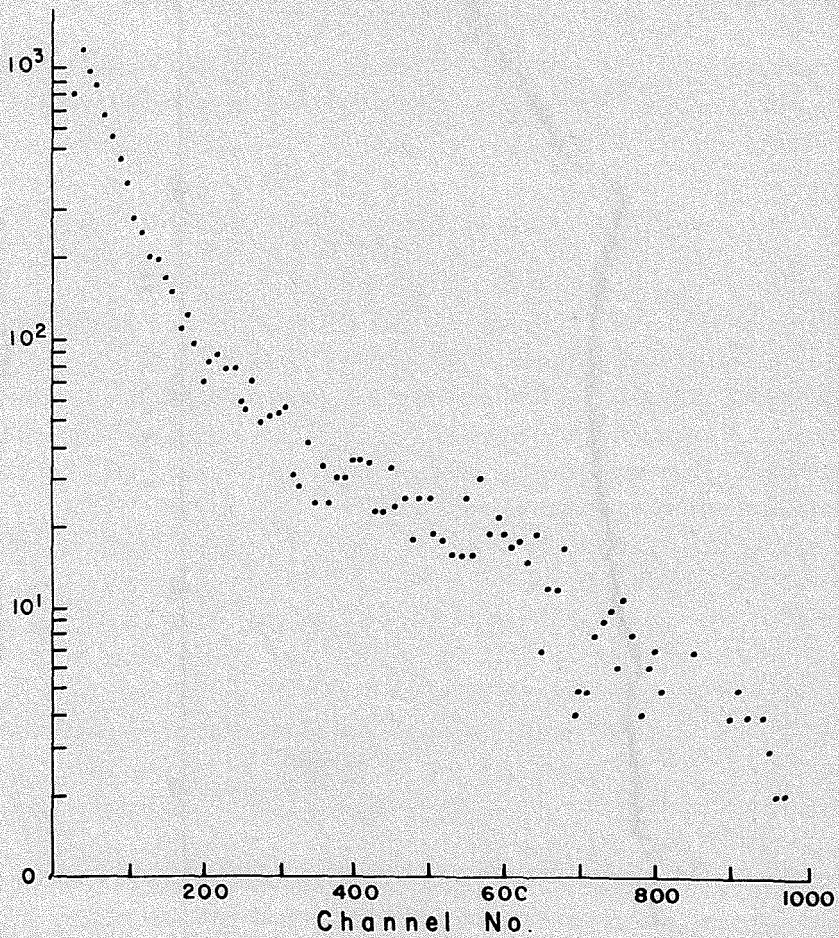


Fig. 2 A typical γ -ray background spectrum taken with a blank specimen (Exposure time: about 190 minutes).

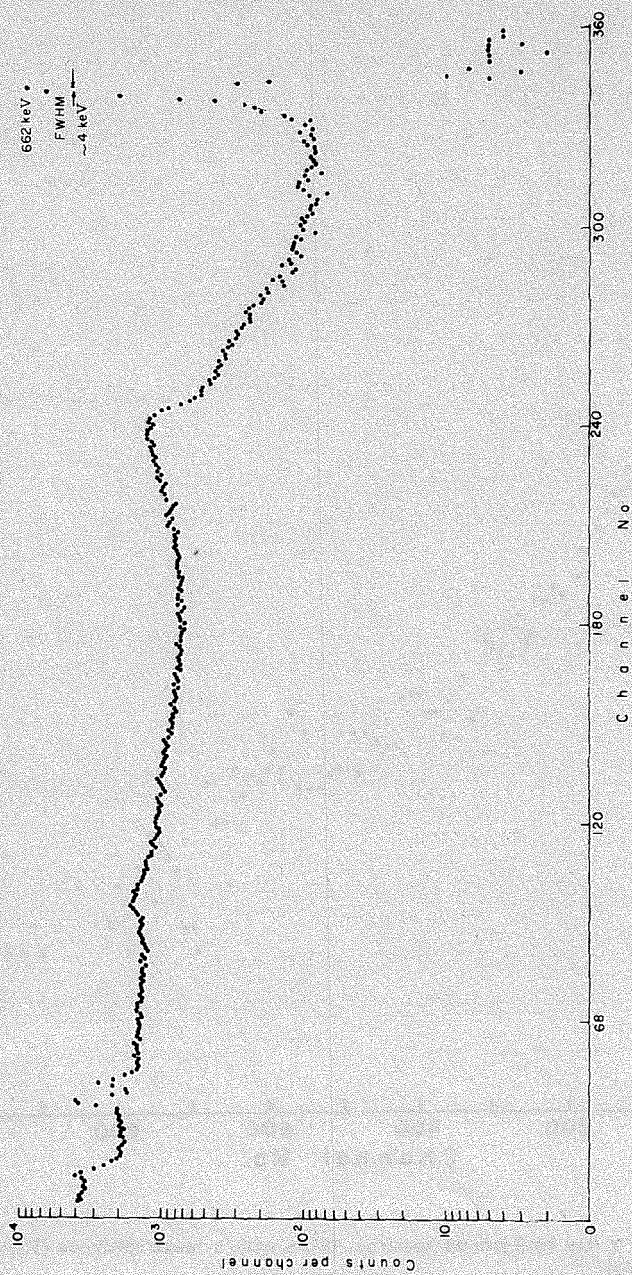


Fig. 3 A γ -ray spectrum of ^{137}Cs 662 keV γ rays.

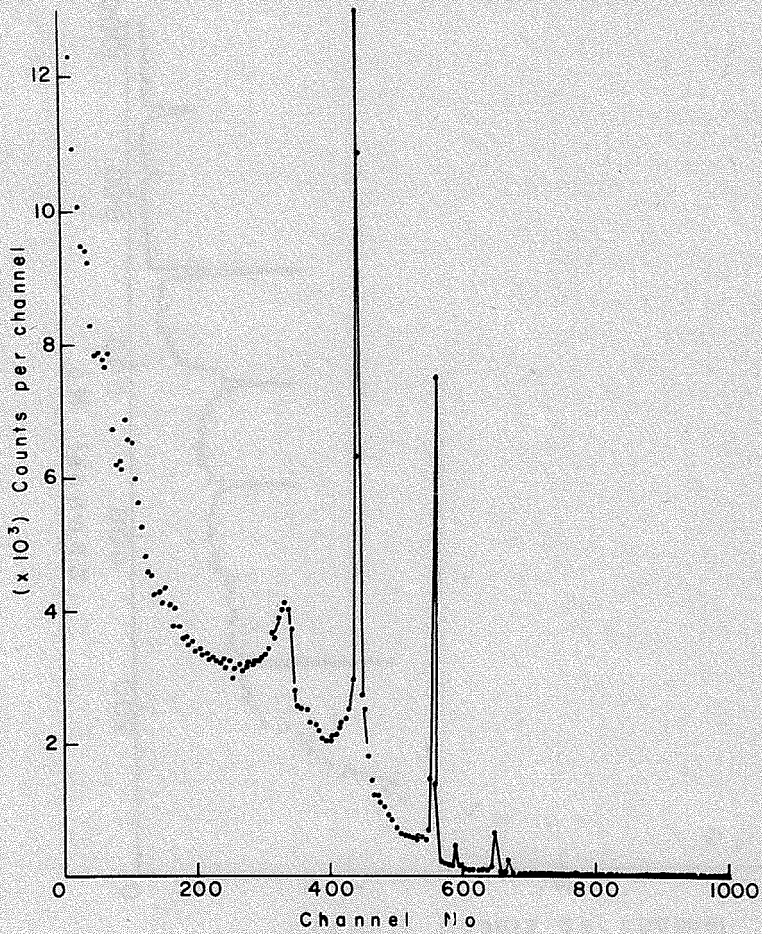


Fig. 4 A γ -ray spectrum of W-1 (diabase) taken 29 days after a 3 hours irradiation (counting time: 20 min.).

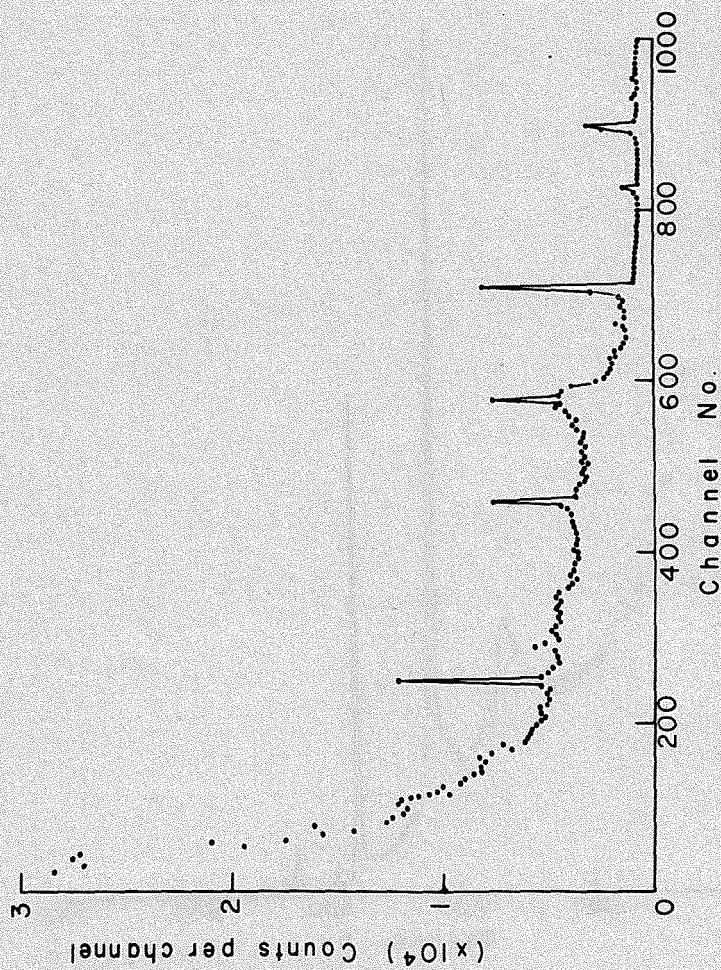


Fig. 5 A γ -ray spectrum of AGV-1 (andesite) taken 7 days after a 40 min. irradiation (counting time: 50 min.).

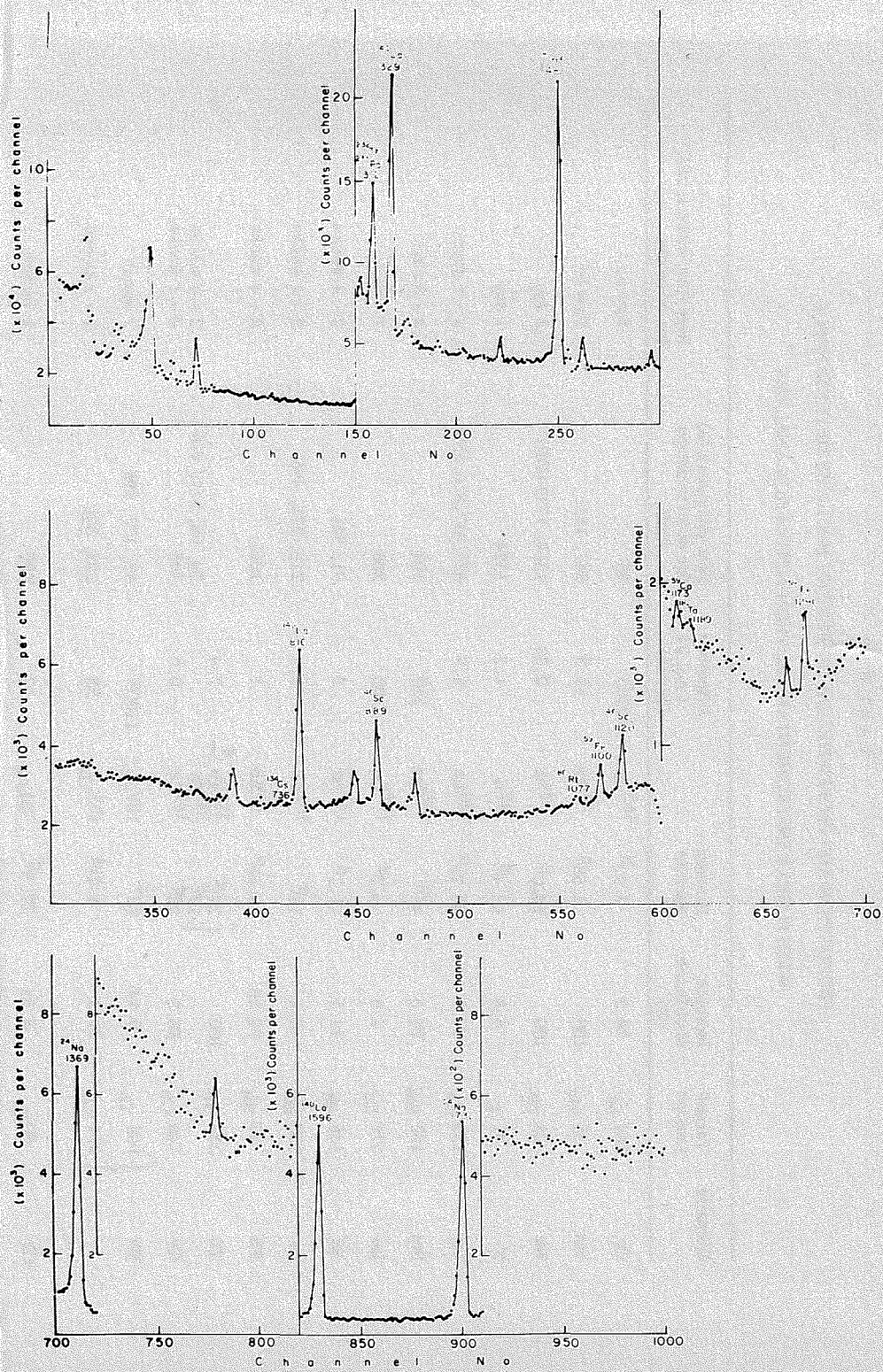


Fig. 6 An expanded version of γ -ray spectrum of G-2 (granite) taken 8 days after 40 min. irradiation (Exposure time: 70 min.)

T A B L E 2

 PRODUCTION AND PROPERTIES OF DIFFERENT NUCLIDES DETERMINABLE
 WITH PURELY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS *

| Element | Target isotope | Isotopic abundance (%) | Product nuclide | Effective (σ_{th}, γ) (barns) | Best photopeak (s) for determination (keV) | Best time after irradiation for counting | |
|---------|--|------------------------|--|---|--|--|------------------------|
| Dy | ^{164}Dy | 28.2 | ^{165}Dy 2.32 ^h | ~ 2700 | 95 | Few hr. | |
| Mn | ^{55}Mn | 100 | ^{56}Mn 2.58 ^h | 13.3 | 847, 1811 | Few hr. | |
| Na | ^{23}Na | 100 | ^{24}Na 15.0 ^h | 0.53 | 1369, 1732 (DE) | 1 day | |
| K | ^{41}K | 6.8 | ^{42}K 12.4 ^h | 1.2 | 1524 | 1 day | |
| La | ^{139}La | 99.9 | ^{140}La 40.22 ^h | 8.9 | 329, 487, 816, 1596 | 4 - 5 days | |
| Sm | ^{152}Sm | 26.6 | ^{153}Sm 47 ^h | 210 | 103 | 4 - 5 days | |
| Lu | ^{176}Lu | 2.6 | ^{177}Lu 6.7 ^d | 2100 | 208 | 2 weeks | |
| Ni | ^{146}Ni | 17.1 | ^{147}Ni 11.1 ^d | 2 | 91, 531 | 2 - 4 weeks | |
| Ba | ^{130}Ba | 0.1 | ^{131}Ba 12 ^d | 8.8 | 216, 373, 496 | 2 - 4 weeks | |
| Rb | ^{85}Rb | 72.15 | ^{86}Rb 18.66 ^d | 1 | 1077 | 2 - 4 weeks | |
| Th | ^{232}Th | 100 | ^{233}Th ^{233}Pa ^{233}U | 7.4 | 94, 98, 312, 416 } 145 } | 2 - 4 weeks | |
| Ce | ^{140}Ce | 88.5 | ^{141}Ce 33 ^d | 0.6 | | | 2 - 4 weeks |
| Yb | ^{168}Yb ^{174}Yb | 0.14 31.8 | ^{169}Yb 32 ^d ^{175}Yb 4.21 ^d | 11000 55 | | 63, 177, 198 283, 396 | 1 month 1 - 2 weeks |
| Cr | ^{50}Cr | 4.31 | ^{51}Cr 27.8 ^d | 17 | 320 | 1 month | |

| | | | | | | | |
|----|-------|-------|--------------------|--------|------|----------------|-------------|
| Fe | 153Eu | 52.2 | 9.3 ^h | 152mEu | 2800 | 122, 842, 963 | 0.5 - 1 day |
| | 58Fe | 0.31 | 45 ^d | 59Fe | 1.1 | 1100, 1291 | Few months |
| Sb | 121Sb | 57.25 | 2.8 ^d | 122Sb | 6 | 566 | 1 week |
| | 123Sb | 42.75 | 60 ^d | 124Sb | 3.3 | 1691 | Few months |
| Tb | 159Tb | 100 | 72.1 ^d | 160Tb | 46 | 299, 963 + 966 | Few months |
| Sc | 45Sc | 100 | 83.9 ^d | 46Sc | 23 | 889, 1120 | Few months |
| Zr | 94Zr | 17.4 | 65 ^d | 95Zr → | 0.08 | 725, 757 | Few months |
| | | | 35.3 ^d | 95Nb | | 766 | |
| Ta | 182Ta | 99.99 | 115.1 ^d | 182Ta | 21 | 68, 100, 1122 | Few months |
| Tm | 169Tm | 100 | 130 ^d | 170Tm | 125 | 84 | Few months |
| Gd | 152Gd | 0.2 | 242 ^d | 153Gd | <180 | 97, 103 | Few months |
| Cs | 133Cs | 100 | 2.05 ^y | 134Cs | 31 | 605, 796 | Few months |
| Co | 59Co | 100 | 5.26 ^y | 60Co | 37 | 1173, 1332 | Few months |

* After Gordon et al (1968)

standard activity for that nuclide.

Below are discussed very briefly some of the interesting points associated with the determinations of different elements.

Sodium, Potassium and Manganese

These elements can be better determined through short irradiations of approximately 5 to 10 minutes duration (depending on the neutron flux available) followed by counting during first few hours or days. As short irradiations were not carried out, these elements could not be determined. Nevertheless, sodium could still be determined even through long irradiations, mainly due to its high sensitivity and relatively long half-life. The measurements were based on 1369 keV line as well as on 1732 keV double-escape (DE) line. Another point of interest probably is that Na measurements suffer from the interfering reaction $^{27}\text{Al} (n, \alpha)^{24}\text{Na}$, which might be important in rocks high in Al content and low in Na. In the present analysis, the Na values agree very well with the flame photometric measurements, (within $\pm 5\%$). This probably goes to indicate that in these cases the interfering reaction is not so important.

Rubidium

There is practically no problem in the determination of rubidium from the 1077 keV line of ^{86}Rb in the spectra taken 2-4 weeks after the long irradiations. There is apparently no interference from other peaks – the nearest peak is that of 1086 keV ^{152}Eu ; but the Compton edge of 1291 keV ^{59}Fe makes the Rb determinations rather difficult in rocks with high Fe content. Further, the sensitivity for Rb determinations in rocks is rather low (lower limit ~ 40 ppm).

Cesium

Cesium can be determined from spectra taken a few months after irradiation. The 605 keV line suffers from a serious interference by

603 keV ^{124}Sb which makes it necessary to correct for this interference or to wait several months for the 60 days ^{124}Sb activity to decay considerably.

On the other hand, the 796 keV line is apparently free from interference and therefore was employed in the present work.

Barium

The 216 keV line needs to be corrected for the ^{160}Tb line of the same energy. In the present work, the 496 keV line was used for barium estimates, but the statistical errors were rather high ($\sim 10\%$) for Ba mainly due to its low sensitivity.

Cobalt

The precision of cobalt determinations is very high. The 1332 keV line is free from interference, while the 1173 keV line suffers from a small interference of 1178 keV ^{160}Tb line. This interference in general may not be of great significance except for samples with rather low values of Co/Tb ratio. Nevertheless, the area of 1173 keV peak was calculated using 4 channels towards the lower side. The 1332 keV line probably yields better results for cobalt determinations.

Iron

The iron determinations are relatively simple. The 1100 keV as well as 1291 keV line can be used. Further, the 835 keV line from 303 days ^{54}Mn produced by ^{54}Fe (n, p) can also be employed.

Scandium

The two lines, 889 and 1120 keV, are very strong in all the spectra, but both of them have problems; the 889 keV falls at the Compton

edge of the 1120 keV peak and the 1120 keV has interference from 1122 keV ^{182}Ta , 1115 keV ^{160}Tb , 1112 keV ^{152}Eu and probably from 1115 keV ^{65}Zn .

For these reasons, the measurements from the 2009 keV sumpeak in Na I (TI) spectra are probably more accurate than those in Ge (Li) spectra (Gordon et al, 1968).

Chromium

The 320 keV line from ^{51}Cr suffers from the interference of the strong 312 keV peak of ^{233}Pa produced by ^{232}Th . The results of Cr determinations are thus less accurate when the Cr/Th ratio is relatively low.

Lanthanum

One observes several distinct lines — 329, 487, 816 and 1596 keV, etc. The 329 keV falls at the Compton edge of 487 keV ^{140}La and the 487 keV suffers in turn from the interference of 482 keV ^{181}Hf and possibly 487 keV ^{131}Ba . In the present work, the 816 and 1596 keV lines were used for La abundance determinations.

Europium

The Eu abundance can be determined from spectra taken either 0.5 — 1 day after irradiation or a few months later. This element has a number of peaks but most of them suffer from interference of other elements. In the present work, the 1408 keV line was employed which appears to be free from interference. The 779 keV ^{152}Eu line could also be used.

Thorium

Th produces 27 day ^{233}Pa which emits a number of gamma rays but

almost all of them suffer from interference. The 312 keV line appeared to be most suitable for the abundance determinations of thorium (although it has interference from 308 keV ^{169}Yb and 320 keV ^{51}Cr lines). In rocks like DTS-1 or PCC-1 with very low Th/Cr, it was rather difficult to estimate the Th contents.

Zirconium

The 725 keV line has rather serious interference from 723 keV ^{154}Eu . Also the 757 keV ^{154}Eu line falls over the zirconium line of the same energy. Thus the 766 line is perhaps the one most suitable for the estimation of Zr abundance.

Hafnium

The Hf contents were determined using the 482 keV line although it suffers from a small interference of 487 keV ^{140}La and 487 keV ^{131}Ba lines. One could also employ the 133 keV line from hafnium with a LEPS high-resolution detector.

Antimony

The Sb abundances were determined using the 1691 keV ^{124}Sb line but are not very accurate because of the line being rather weak in our spectra.

Terbium

Although well-defined peaks of terbium were found in our spectra, all of them suffer from serious interferences of other elements. It was found necessary to have "monitor" spectra in order to correct for them and thus determine the Tb abundances.

Various

Abundances of several other elements such as Cerium, Dysprosium, Lutecium, Gadolinium, Samarium, Neodymium, Thulium, Ytterbium, etc., can be estimated with a LEPS detector (Gordon et al, 1968; Hertogen and Gijbels, 1971).

RESULTS AND DISCUSSION

Table 3 gives the results of analysis in the standard rock samples. It is to be noted that our results, although still preliminary, agree well with those of other workers. Neutron activation data for a few elements in some of these standard rocks is probably being presented for the first time (Fe, Ba and Zr in PCC-1 and DTS-1). For W-1, the results are compared with those reported by Fleischer (1965), while for the rest they are compared with those compiled by Flanagan (1969). Average values for these standards are also given in Flanagan (1972). The range of reported abundance values are given in parenthesis below the corresponding recommended mean values.

In Tables 4 and 5 are presented the results on samples from several geological formations of Mexico (especially from the Guanajuato region).

A mere glance on the data on different rock types shows, as generally expected, a wide variation in elemental abundances for major as well as trace elements determined in this study. Perhaps of more interest are some of the elemental abundance ratios of geochemically related elemental pairs. These ratios are given in Tables 6 and 7 for the U.S.G.S. standard rocks and Mexican rocks, respectively. An excellent review of the application of trace element data to problems of petrology is given by Taylor (1965).

Both K and Na are major elements in most igneous rocks and the K/Na ratios vary between 0.2 and 4 depending upon the type of rock (Daly, 1933; Nockolds, 1954). The few K/Na ratios measured in

T A B L E 3

CONCENTRATION OF SOME ELEMENTS IN STANDARD ROCKS
(CONCENTRATION IN ppm IF NOT INDICATED %)

| Element | G - 2 | G S P - 1 | A G V - 1 | P C C - 1 | D T S - 1 | B C R - 1 | W - 1 |
|------------------|-------------------|-------------------|-------------------|---------------------------------------|---------------------------------------|-------------------|---------------|
| Na (%) | | | | | | | |
| This work | 3.08 * | 2.14 ± 0.06 | 3.16 ± 0.05 | 0.01 ₃ ± 0.002 | 0.01 ₆ ± 0.002 | 2.03 ± 0.04 | 1.56 ± 0.03 |
| Other ** | 3.08 | 2.13 ₇ | 3.21 ₆ | 0.03 ₉ | 0.03 ₄ | 2.45 ₈ | 1.54 |
| | (2.35 - 3.15) | (1.70 - 2.15) | (2.68 - 3.34) | (0.00 - 0.04) | 0.00 - 0.05) | (1.52 - 2.58) | (1.48 - 1.76) |
| K (%) | | | | | | | |
| Flame photometry | 3.30 ± 0.05 | 4.15 ± 0.08 | 2.36 ± 0.05 | 0.01 ₄ ± 0.00 ₅ | 0.01 ₃ ± 0.00 ₅ | 1.41 ± 0.04 | 0.54 ± 0.03 |
| Other | 3.74 ₄ | 4.55 ₆ | 2.40 ₆ | 0.01 ₆ | 0.01 ₉ | 1.39 ₈ | 0.53 |
| | (3.25 - 3.98) | (3.60 - 4.72) | (1.99 - 2.65) | (0.00 - 0.30) | (0.00 - 0.33) | (1.16 - 1.68) | (0.44 - 0.60) |
| Rb | | | | | | | |
| This work | 234 * | 211 ± 22 | <60 | <30 | <30 | 159 ± 18 | <60 |
| Other | 234 | 343 | 89.4 | 0.5 | 2.8 | 72.8 | 22 |
| | (108 - 513) | (200 - 690) | (68 - 130) | (0.05 - <100) | (0.01 - <100) | (45 - 150) | (18 - 93) |

| Element | G - 2 | GSP - 1 | AGV - 1 | PCC - 1 | DTS - 1 | BCR - 1 | W - 1 |
|-----------|---------------|---------------|---------------|---------------|---------------|----------------|---------------|
| Cs | | | | | | | |
| This work | 1.5* | | | <0.2 | <0.2 | 1.8 ± 0.4 | 0.6 ± 0.1 |
| Other | 1.5 | 1.7 | 1.2 | 0.08 | 0.05 | 1.2 | 1.1 |
| | (1.2 - 2) | (0.8 - 3) | (1.13 - 1.4) | (0.02 - 0.08) | (0.02 - 0.05) | (0.95 - 1.6) | (0.5 - 2.3) |
| Ba | | | | | | | |
| This work | 1950* | 610 ± 50 | 1230 ± 90 | <200 | <200 | 330 ± 40 | 250 ± 40 |
| Other | 1950 | 1360 | 1410 | 6.9 | 6.3 | 790 | 180 |
| | (1500-3000) | (855-2000) | (1047-2700) | (<2 - <30) | (<2 - <30) | (480-1230) | (130 - 257) |
| Th | | | | | | | |
| This work | 25.2* | 88 ± 2 | 6.7 ± 0.2 | n.d. | n.d. | 5.5 ± 0.2 | 2.2 ± 0.1 |
| Other | 25.2 | 110.6 | 6.96 | 0.0108 | 0.0092 | 6.81 | 2.4 |
| | (21 - 30) | (99 - 125) | (5 - 10) | (0.0108 - 5) | (0.0092 - <5) | (5 - 15) | (1.3 - 3.2) |
| Fe | | | | | | | |
| This work | 2.1 ± 0.1 | 3.3 ± 0.2 | 4.4 ± 0.2 | 6.7 ± 0.2 | 6.5 ± 0.2 | 9.1 ± 0.3 | 7.78* |
| Other | 1.18 | 3.04 | 4.75 | 5.83 | 6.13 | 9.50 | 7.78 |
| | (1.63 - 2.16) | (2.72 - 3.34) | (4.48 - 5.10) | (5.40 - 6.69) | (5.57 - 6.77) | (8.74 - 10.10) | (7.45 - 8.37) |
| Sc | | | | | | | |

| | | | | | | | | | | | | | | |
|-----------|----------------|---------------|----------------|-------------------|-------------------|----------------|---------------|--------------|-----|-------------|------|-------------|-----|-------------|
| Uiner | 3.9 | (< 2 - 10) | 9.2 | (5.6 - 28) | 13.3 | (8 - 20) | 8.7 | (< 1 - 11) | 3.8 | (< 2 - 5) | 36.3 | (30 - 50) | 3.4 | (33 - 49) |
| Co | | | | | | | | | | | | | | |
| This work | 5.6 ± 0.5 | 4.3 ± 0.4 | 10.7 ± 0.7 | 110 ± 4 | 132 * | 30 ± 2 | 42 ± 2 | | | | | | | |
| Other | 4.9 | 7.5 | 15.5 | 112 | 132 | 35.5 | 50 | | | | | | | |
| | (2 - 21) | (< 3 - 22) | (10 - 30) | (80 - 300) | (96 - 200) | (29 - 60) | (25 - 53) | | | | | | | |
| Cr | | | | | | | | | | | | | | |
| This work | 6.0 ± 0.7 | 8.7 ± 0.8 | 4.8 ± 0.9 | 3090 * | 4560 ± 90 | 9.8 ± 0.7 | 120 ± 3 | | | | | | | |
| Other | 9.0 | 13.2 | 12.9 | 3090 | 4230 | 16.3 | 120 | | | | | | | |
| | (5 - 29) | (5 - 18) | (7 - 45) | (1840 - 4780) | (2840 - 5560) | (8 - 45) | (110 - 160) | | | | | | | |
| La | | | | | | | | | | | | | | |
| This work | 102 ± 6 | 206 ± 7 | 42.6 * | n.d. | n.d. | 25.4 ± 1.2 | 11.6 ± 0.5 | | | | | | | |
| Other | 112 | 280 | 42.6 | < 0.5 | < 0.5 | 28.8 | 20 | | | | | | | |
| | (76 - 300) | (160 - 450) | (25 - 80) | (< 0.5 - < 100) | (< 0.5 - < 100) | (22 - 36) | (9.3 - 30) | | | | | | | |
| Eu | | | | | | | | | | | | | | |
| This work | 1.5 * | | | < 0.05 | < 0.05 | | 0.91 ± 0.09 | | | | | | | |
| Other | 1.5 | 3.1 | 1.7 | < 0.002 | < 0.002 | 2.2 | 1.1 | | | | | | | |
| | (1.37 - 1.6) | (2.0 - 3.5) | (1.55 - 1.7) | — | — | (1.95 - 2.3) | (0.96 - 2) | | | | | | | |
| Zr | | | | | | | | | | | | | | |
| This work | 316 * | | | < 50 | < 50 | | 106 ± 15 | | | | | | | |

| Element | G - 2 | GSP - 1 | AGV - 1 | PCC - 1 | DTS - 1 | BCR - 1 | W - 1 |
|-----------|-----------------|--------------|--------------|-------------------|-------------------|--------------|-------------|
| Other | 316 | 544 | 227 | — | — | 185 | 100 |
| | (250 - 400) | (323 - 685) | (186 - 315) | ($< 2 - < 100$) | ($< 2 - < 100$) | (144 - 275) | (70 - 160) |
| Hf | | | | | | | |
| This work | 7.5* | 13.2 ± 0.2 | 4.2 ± 0.1 | 0.02 ± 0.002 | 0.04 ± 0.004 | 2.6 ± 0.1 | 1.2 ± 0.1 |
| Other | 7.5 | 12.4 | 5.1 | 0.06 | 0.03 | 4.4 | 1.5 |
| | (6.1 - 8.4) | (9.7 - 15) | (3.7 - 6.6) | — | — | (3.3 - 5.4) | (1.5 - 2.0) |
| Ta | | | | | | | |
| This work | 0.9* | 2.1 ± 0.4 | 1.0 ± 0.2 | < 0.3 | < 0.3 | 0.7 ± 0.1 | 0.6 ± 0.1 |
| Other | 0.91 | 1.1 | 0.66 | < 0.1 | < 0.1 | 0.88 | 0.7 |
| | (0.82 - 1.0) | (0.77 - 1.4) | (0.32 - 1.0) | — | — | (0.86 - 0.9) | (0.5 - 0.7) |
| Sb | | | | | | | |
| This work | < 0.2 | | | 1.0* | 0.7 ± 0.2 | | 0.7 ± 0.2 |
| Other | 0.053 | 2.77 | 4.09 | 0.97 | 0.48 | 0.59 | 1.1 |
| | (0.015 - 0.063) | (1.38 - 4.1) | (2.21 - 5.2) | (0.005-1.39) | (0.4 - 0.5) | (0.32 - 1.1) | (0.3 - 1.2) |

* Signifies adopted value for this sample

** The data for comparison have been taken from the compilations by Flanagan (1969) on the second series of standard rocks (G - 2 through BCR-1) and Fleischer (1965) on the first series of standard rocks (G - 1 and W - 1).

Blanks in the table correspond to the element in that sample for which quantitative measurements could not be obtained because of the lack of γ - spectra of suitable time-intervals.

TABLE 4

CONCENTRATIONS OF SOME ELEMENTS DETERMINED IN MEXICAN ROCKS

(Concentration in ppm if not indicated %)

| Sample No. | Rock-type | Na % | K* % | Rb | Cs | Ba | Th | Fe % | Sc |
|------------|---------------------------|--------------|--------------|----------|------------|------------|------------|--------------|------------|
| 7205 | El Cedro Andesite | | 1.61 ± 0.05 | 35 ± 8 | 13.9 ± 0.7 | 320 ± 30 | 7.9 ± 0.1 | 3.78 ± 0.07 | 14.3 ± 0.2 |
| 7212 | Calderon Andesite | 1.71 ± 0.04 | 3.55 ± 0.10 | 290 ± 24 | 7.5 ± 0.7 | 1240 ± 90 | 6.8 ± 0.2 | 1.64 ± 0.07 | 2.7 ± 0.1 |
| 7216 | Calderon Andesite | | 3.36 ± 0.08 | 172 ± 21 | 27 ± 1 | 580 ± 40 | 9.5 ± 0.2 | 1.58 ± 0.05 | 3.3 ± 0.1 |
| 7228 | La Bufa Rhyolite | | 2.45 ± 0.05 | 81 ± 15 | 6.4 ± 0.4 | 1400 ± 100 | 14.8 ± 0.2 | 2.77 ± 0.06 | 16.7 ± 0.3 |
| 7244 | La Bufa Rhyolite | | 3.20 ± 0.08 | 260 ± 30 | 7.7 ± 0.4 | 790 ± 60 | 8.8 ± 0.1 | 1.89 ± 0.04 | 3.3 ± 0.1 |
| 7208 | La Bufa Rhyolite | 2.07 ± 0.04 | 3.86 ± 0.12 | 283 ± 22 | 3.1 ± 0.3 | 820 ± 50 | 6.7 ± 0.2 | 1.32 ± 0.06 | 2.4 ± 0.1 |
| 7221 | Granite-diorite intrusive | 3.01 ± 0.05 | 0.61 ± 0.03 | 74 ± 10 | 1.1 ± 0.2 | <200 | 0.7 ± 0.05 | 1.84 ± 0.10 | 5.3 ± 0.2 |
| 7222 | Red conglomerate | 1.65 ± 0.03 | 0.22 ± 0.02 | 110 ± 13 | 3.7 ± 0.4 | <200 | — | 6.78 ± 0.21 | 26.0 ± 0.5 |
| 7234 | Limestone | 2.11 ± 0.03 | 0.15 ± 0.01 | 63 ± 8 | 0.9 ± 0.1 | <200 | 0.2 ± 0.02 | 6.19 ± 0.18 | 26.5 ± 0.5 |
| 7225 | Limestone | 0.06 ± 0.002 | 0.30 ± 0.02 | <30 | 0.7 ± 0.1 | <200 | 1.7 ± 0.1 | 2.79 ± 0.09 | 2.1 ± 0.1 |
| 7232 | Shale | | 2.05 ± 0.06 | 117 ± 10 | 5.7 ± 0.4 | 2460 ± 140 | 4.2 ± 0.1 | 4.27 ± 0.08 | 34.4 ± 0.5 |
| 7220 | Shale | | 2.31 ± 0.05 | 157 ± 18 | 7.4 ± 0.5 | 2890 ± 160 | 5.9 ± 0.1 | 4.54 ± 0.08 | 17.9 ± 0.3 |
| 7225 | Shale | 0.35 ± 0.05 | 2.44 ± 0.03 | 142 ± 17 | 8.2 ± 0.9 | 960 ± 70 | 8.8 ± 0.2 | 4.69 ± 0.18 | 14.4 ± 0.3 |
| 7203 | Dyke rock | 1.92 ± 0.05 | 3.39 ± 0.09 | 136 ± 14 | 8.0 ± 0.8 | 850 ± 50 | 9.9 ± 0.2 | 2.75 ± 0.10 | 10.2 ± 0.2 |
| 7217 | Dyke rock | 0.50 ± 0.01 | 2.04 ± 0.05 | 117 ± 16 | 11 ± 1 | <200 | 1.2 ± 0.1 | 2.53 ± 0.10 | 8.9 ± 0.2 |
| 7238 | Mineral vein | 1.44 ± 0.04 | 0.04 ± 0.005 | 149 ± 16 | 2.8 ± 0.4 | <200 | 1.5 ± 0.1 | 11.26 ± 0.31 | 39.6 ± 0.7 |
| 7101 | Basaltic lava | | 1.05 ± 0.02 | 56 ± 10 | 0.3 ± 0.05 | 280 ± 40 | 1.8 ± 0.1 | 3.77 ± 0.08 | 14.0 ± 0.3 |
| 7102 | Chlorite-Andesite | | 2.18 ± 0.07 | 46 ± 8 | 0.3 ± 0.05 | 220 ± 40 | 6.1 ± 0.2 | 5.34 ± 0.10 | 21.6 ± 0.4 |

TABLE 5

CONCENTRATION OF SOME MORE ELEMENTS DETERMINED IN MEXICAN ROCKS

(Concentrations in ppm if not indicated %)

| Sample No. | Rock-type | Co | Cr | La | Eu | Zr | Hf | Ta | Sb |
|------------|---------------------------|------------|------------|------------|------------|----------|-------------|------------|------------|
| 7205 | El Cedro Andesite | 8.8 ± 0.6 | 24 ± 1 | | 2.0 ± 0.1 | 240 ± 20 | 5.9 ± 0.2 | 0.5 ± 0.2 | 0.5 ± 0.2 |
| 7212 | Calderon Andesite | 1.5 ± 0.1 | 5.2 ± 0.7 | 11.9 ± 0.6 | | | 0.82 ± 0.03 | <0.1 | |
| 7216 | Calderon Andesite | 0.4 ± 0.1 | 7.9 ± 0.9 | | 0.7 ± 0.1 | 210 ± 20 | 2.8 ± 0.1 | 1.6 ± 0.2 | 0.3 ± 0.1 |
| 7228 | La Bufa Rhyolite | 1.7 ± 0.3 | 10.6 ± 0.7 | | 2.8 ± 0.2 | 320 ± 30 | 10.2 ± 0.3 | 1.3 ± 0.2 | 0.8 ± 0.3 |
| 7244 | La Bufa Rhyolite | 0.9 ± 0.2 | 7.3 ± 0.9 | | 0.4 ± 0.05 | 155 ± 15 | 3.1 ± 0.1 | 1.2 ± 0.2 | 0.1 ± 0.05 |
| 7208 | La Bufa Rhyolite | 2.6 ± 0.3 | 9.1 ± 0.5 | 14.4 ± 0.7 | | | 0.83 ± 0.02 | 0.6 ± 0.1 | |
| 7221 | Granite-diorite intrusive | 5.3 ± 0.7 | — | 5.1 ± 0.3 | | | 0.40 ± 0.01 | 1.6 ± 0.3 | |
| 7222 | Red conglomerate | 25 ± 2 | 137 ± 3 | 8.3 ± 0.8 | | | 0.54 ± 0.02 | <0.1 | |
| 7234 | Limestone | 31 ± 2 | 447 ± 5 | 6.4 ± 0.4 | | | 0.49 ± 0.01 | 1.0 ± 0.2 | |
| 7226 | Limestone | 5.5 ± 0.5 | 24.5 ± 0.8 | 9.1 ± 0.5 | | | 0.61 ± 0.01 | <0.1 | |
| 7232 | Shale | 3.8 ± 0.4 | 6.7 ± 0.9 | | 2.1 ± 0.2 | 460 ± 40 | 5.9 ± 0.2 | 0.7 ± 0.1 | 1.7 ± 0.4 |
| 7220 | Shale | 14.5 ± 0.8 | 78 ± 2 | | 1.7 ± 0.1 | 160 ± 15 | 3.3 ± 0.1 | 0.3 ± 0.1 | 2.6 ± 0.6 |
| 7225 | Shale | 9.1 ± 0.7 | 80 ± 2 | 29 ± 1 | | | 1.00 ± 0.02 | 0.1 ± 0.05 | |
| 7203 | Dyke rock | 1.2 ± 0.3 | 1.3 ± 0.2 | 42 ± 2 | | | 2.50 ± 0.05 | <0.1 | |
| 7217 | Dyke rock | 5.4 ± 0.5 | 29 ± 1 | 30 ± 2 | | | 3.63 ± 0.06 | 2.1 ± 0.3 | |
| 7238 | Mineral vein | 37 ± 2 | 87 ± 2 | 2.4 ± 0.1 | | | 0.10 ± 0.01 | 0.3 ± 0.1 | |
| 7101 | Basaltic lava | 11.9 ± 0.8 | 42 ± 2 | | 1.2 ± 0.1 | 130 ± 15 | 2.7 ± 0.1 | 0.2 ± 0.1 | 0.4 ± 0.2 |
| 7102 | Chlorite - Andesite | 19.0 ± 0.9 | 123 ± 2 | | 2.3 ± 0.2 | <20 | 5.0 ± 0.1 | 0.1 ± 0.05 | 0.4 ± 0.2 |

TABLE 6

VARIOUS ELEMENTAL RATIOS

Standard Rocks

| Ratio Standard Rock | K/Na | K/Rb | (K/Cs) $\times 10^{-3}$ | Ba/Rb | Ba/Cs | (K/Th) $\times 10^{-3}$ | (Fe/Sc) $\times 10^{-3}$ | Zr/Hf | Hf/Ta |
|---------------------------|------|------|----------------------------|-------|-------|----------------------------|-----------------------------|-------|-------------------|
| G - 2 | 1.07 | 141 | 22 | 8.3 | 1300 | 1.3 | 5.5 | 42 | 8.3 |
| GSP - 1 | 1.94 | 197 | | 2.9 | | 0.47 | 6.2 | | 6.3 |
| AGV - 1 | 0.75 | >393 | | >21 | | 3.5 | 4.3 | | 4.2 |
| PCC - 1 | 1.08 | >5 | >0.7 | | | | 7.7 | <2500 | >0.07 |
| DTS - 1 | 0.81 | >4 | >0.7 | | | | 1.8 | <1250 | >0.1 ₃ |
| BCR - 1 | 0.69 | 89 | 7.8 | 2.1 | 183 | 2.6 | 3.5 | | 3.7 |
| W - 1 | 0.35 | >90 | 9.0 | >4.2 | 417 | 2.5 | 2.3 | 88 | 2.0 |

T A B L E 7
 VARIOUS ELEMENTAL RATIOS
 Mexican rocks

| Ratio | K/Na | K/Rb | (K/Cs) $\times 10^{-3}$ | Ba/Rb | Ba/Cs | (K/Th) $\times 10^{-3}$ | (Fe/Sc) $\times 10^{-3}$ | Zr/Hf | Hf/Ta |
|------------|------|------|----------------------------|-------|-------|----------------------------|-----------------------------|-------|-------|
| Sample No. | | | | | | | | | |
| 7205 | | 460 | 1.2 | 9.1 | 23 | 2.0 | 2.6 | 41 | 11.8 |
| 7212 | 2.08 | 122 | 4.7 | 4.3 | 165 | 5.2 | 6.1 | 75 | >8.2 |
| 7216 | | 195 | 1.2 | 3.4 | 21 | 3.5 | 4.8 | 31 | 1.8 |
| 7228 | | 302 | 3.8 | 17 | 219 | 1.7 | 1.7 | 50 | 7.8 |
| 7244 | | 136 | 4.2 | 3.0 | 103 | 3.6 | 5.7 | | 2.6 |
| 7208 | 1.86 | 82 | 12.5 | 2.9 | 265 | 5.8 | 5.5 | | 1.4 |
| 7221 | 0.20 | 82 | 5.5 | <2.7 | <182 | 8.7 | 3.5 | | 0.3 |
| 7222 | 0.13 | 20 | 0.6 | <1.8 | <54 | — | 2.6 | | >5.4 |
| 7234 | 0.07 | 24 | 1.7 | <3.2 | <222 | 7.5 | 2.3 | | 0.5 |
| 7226 | 19 | >100 | 4.3 | — | <286 | 1.8 | 13.3 | | >6.1 |
| 7232 | | 175 | 3.6 | 21 | 432 | 4.9 | 1.2 | 78 | 8.4 |
| 7220 | | 147 | 3.1 | 18 | 391 | 3.9 | 2.5 | 49 | 11 |
| 7225 | 7.0 | 172 | 3.0 | 6.8 | 117 | 2.8 | 3.3 | 10 | 10 |
| 7203 | 1.77 | 249 | 4.2 | 6.3 | 106 | 3.4 | 2.7 | | >25 |
| 7217 | 4.1 | 174 | 1.9 | <1.7 | <18 | 17 | 2.8 | | 1.7 |
| 7238 | 0.03 | 3 | 0.14 | <1.3 | <71 | 0.3 | 2.8 | | 0.3 |
| 7101 | | 188 | 35 | 5.0 | 933 | 5.8 | 2.7 | 48 | 13.5 |
| 7102 | | 474 | 73 | 4.8 | 733 | 3.6 | 2.5 | <4 | 50 |

plutonic and effusive rocks of this area are somewhat normal.

On the other hand, the two limestone samples analysed give widely different K/Na ratios mainly due to widely different Na contents, which may perhaps be due to different phase distribution in these samples, because sodium in limestone, as in modern carbonate sediments, is contributed from several phases: feldspar, Na-clay, sea salt and skeletal material (Heier and Billings, 1970a).

Rubidium, a trace element in the earth's crust is very similar in size and chemical character to potassium, with which element it shows a well-known geochemical coherence. The K/Rb ratios are useful as petrogenetic indicators. Most rocks of the continents have K/Rb ratios between 160 and 300, with an average of about 230 (Heier and Adams, 1964). Ratios definitely outside this trend (160-300) call for special explanation. In fact, a covariance analysis of K/Rb fractionation trends by Shaw (1968) has revealed the main trend variation of K/Rb ratio as function that slightly decreases with increasing K content.

The two andesites (El Cedro and Calderon) from the Guanajuato region have distinct K/Rb ratios – El Cedro having considerably higher ratio than the Calderon. Basaltic lava from the Pachuca area has rather low ratio ~ 190 , while Chlorite-Andesite from this area has high K/Rb ratio. Rhyolites and several dyke rocks have, in general, normal ratios. It should, however, be pointed out that further results are needed to confirm the variation trend of K/Rb ratios in these rocks.

One mineral vein sample from the Guanajuato area has excessive Rb enrichment (K/Rb ~ 3); also having a very low K/Na ratio ~ 0.03 only. It may be particularly interesting to investigate this effect further.

The K/Rb ratio in sedimentary rocks shows somewhat interesting variation. There is a notable Rb enrichment in red conglomerate (K/Rb ~ 20). It has been found that K/Rb ratio decreases with weathering (Horstman, 1957).

One limestone sample shows a considerable Rb enrichment (K/Rb ~ 24), while the other sample has a normal K/Rb ratio. Shales from this area give an average K/Rb ratio of about 160, perhaps

suggesting that Rb is rather concentrated relative to K in shales. Such average K/Rb ratios ~ 150 have elsewhere been found in shales (Heier and Adams, 1964).

The geochemical behavior of barium is rather simple as it substitutes only for K^+ among the common cations and is captured in early K-minerals, but on account of the covalent nature of the Ba-O bond, is not depleted until late in the differentiation.

Ba contents of volcanic rocks are quite normal and the mean values are somewhat close to the averages given by Fischer and Puchelt (1972). For limestones and red conglomerate, only qualitative estimates for Ba contents have been obtained, but shales from this area seem to be enriched in Ba (1000 – 3000 ppm), as the reported Ba averages for shales generally vary from 250 to 800 ppm.

Cesium is one of the potentially most useful trace elements (Taylor, 1965). Being the largest cation, it is admitted into lattice positions of potassium and is not enriched until late in a fractional crystallization.

Cs contents of volcanic rocks of Pachuca area, are quite low (~ 0.3 ppm), while igneous rocks from the Guanajuato region show generally high Cs values. The rhyolites have Cs contents close to the estimated Cs average of 5.1 ppm for these rocks (Heier and Adams, 1964), but the andesites are considerably enriched in Cs with 7 to 27 ppm values very much higher than the reported average and individual values (Heier and Billings, 1970b). Among sedimentary rocks, the limestones contain low Cs (~ 1 ppm) as compared to shales (~ 7 ppm) from the same area.

Of particular interest are the K/Cs and Ba/Cs ratios which should decrease with increasing differentiation, as Ba^{2+} is enriched in earlier K-bearing minerals and Cs^+ in the later (Taylor, 1965). In our analysis, the volcanic rocks of Pachuca area show very high K/Cs as well as Ba/Cs ratios, while those from Guanajuato area have considerably lower ratios. A mineral vein sample shows again as for K/Rb ratio, a remarkably low value for K/Cs ratio. These results might have particular bearing on the mineralization in this area and further work on these lines is suggested to be undertaken in order to understand

significance and application of trace element data to such problems.

Thorium is geochemically related to uranium and their geochemistry as well as Th/U ratios are specially useful in understanding various geological and geophysical problems (Rogers and Adams, 1969). The K/Th and K/U ratios are also useful, and in fact, these three elements, viz., U, Th and K are the principal heat-producing elements in the earth.

The Th contents are generally in the observed normal limits for the various rock types. The K/Th ratios in the igneous and sedimentary rocks, though having considerable variation, do not show any special trend. Thus, Heier and Rogers (1963) found a nearly constant value of approximately 3×10^3 for K/Th ratio in a large variety of igneous rocks, while Pliler and Adams (1962) observed this constancy of K/Th ratio in sediments as well as in igneous rocks.

The geochemical behavior of scandium is rather complex. Because of the similarity in size, Sc^{3+} is expected to be captured in Fe^{2+} positions. Our Sc values for igneous rocks are in the general range expected for these rocks (Fron del, 1970). On the other hand, limestones show rather high Sc contents for such rocks, while shales are characterized by normally high values as expected (Turekian and Wedepohl, 1961; Norman and Haskin, 1968). Numerous efforts have been made to correlate Sc abundances with chemical parameters. Thus, Frycklund and Fleischer (1963) have observed a good correlation between Sc and total (Fe^{2+} , Fe^{3+}) for volcanic rocks. Nevertheless, more results are needed to establish whether or not such correlation exists in our case.

The geochemical behavior of cobalt, as that of nickel, is quite diverse and clearly displays the importance of rather small differences in properties. The Co contents of volcanic rocks generally decrease in the sequence basalt-andesite-rhyolite, as expected. Shales from this area have rather normal Co values, while limestones show unusually high values. This unusual concentration in the limestones is also reflected in their Cr contents which are considerably higher than the average value of 10 ppm for these rocks (average abundances given in Taylor, 1965).

The geochemistry of antimony is not very well-known. This is partly due to analytical problems in determining trace quantities of this element. Sb contents of igneous rocks tend to be rather low, while a few samples of shales analysed show somewhat higher values. These conclusions are in accordance with the data on antimony abundance variations given in Onishi (1969).

Zirconium and hafnium are closely associated and the Zr/Hf ratios are useful to understand their geochemical association. Our Zr/Hf ratios are scattered around 50 – a terrestrial ratio, (Fleischer 1955), or 55-ratio for zircons (Taylor, 1965). However more data is needed to establish the existence or otherwise of any definite trend in the abundance of these elements. The Hf/Ta ratio apparently decreases in the sequence basalt-andesite-rhyolite, which is consistent with Taylor (1965); a decrease in this ratio with differentiation.

The elements La, Eu and Ta determined in this study, belong to the so called Lanthanide group La-Lu. The elements of this group have a close chemical behavior and form one of the most interesting groups of elements in geochemistry and cosmochemistry. It would be worthwhile undertaking more detailed studies of the distribution of these elements.

A more detailed study of the Guanajuato Mineral District is now in progress. Further samples are being obtained so that data both on whole rocks and on mineral fractions may supplement available petrogenetic information on this and adjacent provinces.

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