Three polymorphs of silica were identified. Tridymite occurs with cristobalite in 10044 and quartz with cristobalite in 10072, both as fine-grained intergrowths. Such associations are characteristic of terrestrial lavas where rapid cooling has delayed the sluggish inversions to account for the coexistence of high- and low-temperature forms of silica. Tridymite and cristobalite are seldom, if ever, found in deep-seated rocks. Nonequilibrium conditions are indicated for 10072, in which silica occurs with olivine of composition Fa35, but silica is compatible with fayalite in 10044. Aside from these equilibrium considerations, the presence of tridymite indicates that not all of the Apollo 11 rocks were subjected to shock pressures in excess of 3 kb.

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## Gallium, Germanium, Indium, and Iridium in Lunar Samples

Abstract. Neutron activation analyses of gallium, germanium, indium, and iridium in eight lunar samples and in meteorites and rocks (including four calciumrich achondrites and five terrestrial basalts) with similar bulk compositions are reported. Lunar gallium concentrations are remarkably constant at about 5 parts per million, three times higher and four times lower than those in eucritic (calciumrich) achondrites and terrestrial basalts, respectively. Lunar germanium concentrations range from  $\leq$  0.04 to 0.4 part per million. Basaltic achondrites have similar germanium concentrations, whereas those in terrestrial basalts are uniformly higher at about 1.4 parts per million. Concentrations of indium in lunar samples range from 3 to 60 parts per billion, whereas those in terrestrial basalts are 80 to 100 parts per billion, and those in basaltic achondrites 0.4 to 3 parts per billion. Lunar iridium concentrations appear to be in the 0.1 to 10 parts per billion range. The Tranquillitatis samples are distinctly different from calcium-rich achondrites and terrestrial basalts.

In meteorites containing reduced Ni-Fe, Ge and Ir are heavily concentrated in such phases, Ga is slightly concentrated in the metal relative to the silicate fraction, and In is enriched in the sulfide and silicate phases (1). The samples from Mare Tranquillitatis are of basaltic composition, with negligible amounts of reduced Ni-Fe (2). Relative to Si, Ga and In abundances in basaltic terrestrial rocks are similar to those in type 1 carbonaceous chondrites. Germanium and Ir are severely depleted in basalts relative to the chondrites. Reasonably good information is available regarding the geochemical behavior of Ga in basalts; Prinz (3) indicates that Ga concentrates in the plagioclase and that Ga shows no correlation with the crystallization index, which is an indication of the degree of magmatic fractionation. Very little is known about the geochemical behavior of Ge, In, and Ir in basaltic rocks and magmas, mainly because the concentrations of these elements are at or below the detection limits of emission spectrographic analysis. Thus, to provide a meaningful basis for the interpretation of our analyses of the lunar materials, we initiated studies of the basaltic geochemistry of the elements included in our investigations. We report here concentrations of Ga, Ge, and In in eight Apollo 11 samples and initial investigations of these three elements in terrestrial and meteoritic rocks of basaltic composition. Our Ir data need further refinement and are not tabulated.

The elements Ga, Ge, In, and Ir were determined by a neutron activation scheme involving their sequential radiochemical separation. Gold was also determined in the sequence, but will be discussed elsewhere. The techniques are those outlined previously, with minor changes. After the samples were subjected to radiochemical separation,  $\gamma$ spectra were recorded with NaI scintillation detectors [or occasionally a Ge (Li) ionization detector] in conjunction with a multichannel analyzer.

The precision limits of the method at 68 percent confidence when applied to the analysis of L-group chondrites has been given (4) as  $\pm$  3.5, 30, 18, and 8 percent for the elements Ga, Ge, In, and Ir. We have not adequately retested the precision during these analyses, but estimate that our Ga (all values), In (values

Table 1. The Ga, Ge, and In concentrations in lunar surface materials.

| Sample | Petrolog.<br>class | Ga (ppm)   |      | Ge (ppn           | n)    | In (ppb)   |                     |
|--------|--------------------|------------|------|-------------------|-------|------------|---------------------|
|        |                    | Replicates | Mean | Replicates        | Mean  | Replicates | Mean                |
| 10084  | Fines              | 4.4, 4.9   | 4.6  | 0.34. 0.35        | 0.34  | 681 677    | 679                 |
| 10021  | Brec               | 5.7, 5.3   | 5.5  | 0.46. 0.31        | 0.38  | 14 30      | 22 + 8              |
| 10046  | Brec               | 5.6, 5.2   | 5.4  | 0.38. 0.34        | 0.36  | 25 6       | $\frac{22}{16} + 0$ |
| 10048  | Brec               | 5.1, 5.4   | 5.2  | 0.35, 0.29        | 0.32  | 56,65      | 60 - J              |
| 10056  | Brec               | 5.0, 5.1   | 5.0  | $0.02. \leq 0.04$ | <0.04 | 24 35      | 3.0                 |
| 10057  | CrysA              | 5.0, 4.9   | 4.9  | $0.22. \leq 0.08$ | <0.2  | 30 29      | 3.0                 |
| 10060* | Brec               | 4.9, 5.5   | 5.2  | 0.20, 0.24        | 0.22  | 1150 911   | $1030 \pm 150$      |
| 10072  | CrysA              | 4.8, 5.1   | 4.9  | 0.026, 0.085      | ≤0.08 | 49, 54     | 52                  |

\*Ground and split at Manned Spacecraft Center.

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above 1 ppb), and Ir (values greater than 2 ppb) limits are about the same as those previously reported. Our Ge (values above 1 ppm) errors appear to be somewhat lower, amounting to limits of about  $\pm 8$  percent at 68 percent confidence. Concentrations less than those listed are less precise, and some of our lowest results are listed only as upper limits.

The accuracy of our method can best be judged by comparison of our analyses of USGS standard rocks with those of other research groups. Our earlier Ga data (4) on W-1 and a number of Lgroup chondrites agreed quite well with those of Fouché and Smales (5). Our current data on G-2 and BCR-1 average about 15 percent lower than those of Brunfelt et al. (6), and our PCC-1 value is a factor of two lower than their result. There are no reliable results for Ge on the new USGS rock standards, but our earlier Ge data (4) were systematically about 10 percent higher than those of Fouché and Smales (5) and Greenland and Lovering (7). As discussed by Tandon and Wasson (4), our In data are in good agreement with previous results obtained for L-group chondrites and standard rocks, and our current values on the new USGS standards agree well with the concentrations found by Johansen and Steinnes (8). We conclude that our systematic errors are, at worst, no greater in magnitude than the random errors discussed above.

In Table 1 are listed Ga, Ge, and In data on eight lunar samples. Also listed is the rock type (9). Gallium is remarkably uniform in the lunar samples. In fact, the relative standard deviation of an individual result about the grand mean of 5.1 ppm is only 7 percent, and an appreciable fraction of the scatter is



Fig. 1. Chemical data on Hawaiian basalts plotted versus the crystallization index. The Ga and Ge are enriched in the later differentiates, whereas Ge is unaffected by the magmatic fractionation process.

contributed by experimental error. Germanium is much more variable. In the fines and four breccia samples the Ge concentration ranges from 0.2 to 0.4 ppm. In one breccia and in the crystalline rocks the range is from  $\leq 0.04$  ppm to  $\leq 0.2$  ppm. The concentration of In is highly variable. In the fines and in sample 10060 the In concentration was very high, on the order of 1 ppm, but these were quite possibly contaminated by the In seal of the rock box and during the homogenization and splitting process at MSC, respectively. Indium contents of the other lunar rocks ranged from 3 to 60 ppm, with no particular correlation with the type of sample. The agreement of replicates was very poor for two of the breccias. This may reflect sampling inhomogeneities, but may also be contamination effects, and there is the possibility that all samples were contaminated, perhaps by the In seal in the lunar rock box. Our data on Ir are currently not publishable, primarily because of incorrect monitor preparation. The values for the lunar samples range from about 0.1 to about 10 ppb.

In Table 2 are listed Ga, Ge, and In concentrations for four basaltic achondrites and nine terrestrial rocks, including five basalts and four USGS standard rocks. The basaltic achondrites consisted of three eucrites and one howardite. The eucrites showed very uniform Ga concentrations of about 1.7 ppm, and the howardite a lower value of about 0.9 ppm. These are well below the Ga concentration (5.1 ppm) of the Tranquillitatis samples. Germanium concentrations were low and near our detection limit. All achondrite values were less than or equal to 0.15 ppm, about the same as the lowest values observed in the lunar crystalline rocks. Indium concentrations ranged from 0.4 to 3 ppb, and in three of the four meteorites were lower than the lowest lunar results.

In terrestrial mafic and felsic rocks Ga concentrations were about 20 ppm (four times higher than in the mafic lunar rocks), but much lower values were found in terrestrial ultramafic rocks. Germanium was remarkably uniform in all terrestrial rocks that we investigated and averaged about 1.4 ppm. This is more than an order of magnitude higher than the values in basaltic achondrites and in three of the lunar rocks, and five times higher than the highest lunar Ge concentrations. Terrestrial In concentrations range from 3 ppb in peridotite to about 100 ppb in mafic rocks, a range which is comparable to the range ob-

Table 2. Ga, Ge, and In concentrations in Ca-rich achondrites, terrestrial basalts and other terrestrial rocks. The sources are abbreviated as follows: GAM, G. A. MacDonald, University of Hawaii; MHNP, Muséum d'Histoire Naturelle, Paris; UCLA, University of California, Los Angeles; USGS, United States Geological Survey; and UTü, Mineralogisches Institut, Universität Tübingen.

|                        | Туре         | Source | No.   | Ga (ppm)      |      | Ge (ppm)               |       | In (ppb)   |            |
|------------------------|--------------|--------|-------|---------------|------|------------------------|-------|------------|------------|
| Sample                 |              |        |       | Replicates    | Mean | Replicates             | Mean  | Replicates | Mean       |
| Juvinas                | Eucrite      | UTü    |       | 1.8, 1.7, 1.9 | 1.7  | 0.06, <0.09            | ≤0.09 | 1.4, 1.4   | 1.4        |
| Pasamonte              | Eucrite      | UCLA   | 308   | 1.7, 1.7      | 1.7  | $\leq 0.04, \leq 0.01$ | ≤0.04 | 3.4, 3.0   | 3.2        |
| Stannern               | Eucrite      | UTü    |       | 1.6, 2.0, 1.6 | 1.7  | $0.15, \leq 0.02$      | ≤0.15 | 0.27, 0.45 | 0.36       |
| Le Teilleul            | Howardite    | MHNP   | 711   | 0.85, 0.93    | 0.89 | 0.05, 0.09             | 0.07  | 0.88, 0.72 | 0.80       |
| Wajanae. Haw.          | Thol, basalt | GAM    | C-6   | 17.2, 17.2    | 17.2 | 1.4, 1.4               | 1.4   | 85, 69     | 7 <b>7</b> |
| Wajanae, Haw,          | Thol, basalt | GAM    | C-11  | 20.0, 21.1    | 20.6 | 1.9, 1.5               | 1.7   | 95, 78     | 87         |
| Wajanae, Haw.          | Thol, basalt | GAM    | C-20  | 23.1. 19.8    | 22.0 | 1.2, 1.5               | 1.5   | 117, 81    | 99         |
| Wajanae, Haw.          | Alk, basalt  | GAM    | C-31  | 24.1. 26.2    | 25.1 | 1.6, 1.4               | 1.5   | 87, 78     | 82         |
| Wajanae, Haw.          | Hawaiite     | GAM    | C-178 | 2.8, 27.2     | 27.6 | 1.4                    | 1.4   | 108, 115   | 112        |
| Bridal Veil            |              |        |       |               |      |                        |       |            |            |
| Ore.                   | Basalt       | USGS   | BCR-1 | 19.8, 19.9    | 19.8 | 1.4, 1.5               | 1.5   | 98, 94     | 96         |
| Westerly, R.I.         | Granite      | USGS   | G-2   | 22.0, 22.0    | 22.0 | 1.3, 1.1               | 1.2   | 30, 35     | 32         |
| Cazadero, Cal.         | Peridotite   | USGS   | PCC-1 | 0.65, 0.60    | 0.63 | 1.1, 1.0               | 1.0   | 3.4        | 3.4        |
| Twin Sisters,<br>Wash. | Dunite       | USGS   | DTS-1 | 0.46, 4.8     |      | 1.1, 1.0               | 1.0   | 24         | 24         |

served in lunar samples. The terrestrial basalts, however, are distinctly higher in In content than any lunar rocks. The highest Ir values in the lunar samples appear to be about an order of magnitude higher than those observed in basaltic rocks and achondrites.

On the basis of these limited data one can note that the samples collected in Mare Tranquillitatis are distinctly different from the logical comparison materials of Ca-rich (basaltic) achondrites and typical terrestrial rocks of basaltic composition. Our limited conclusions are: (i) Typical basaltic achondrites did not originate in the Mare Tranquillitatis area of the moon; and (ii) the lunar materials of basaltic composition differ from those found on the earth either as a result of differing fractionation processes or differing primitive starting materials, or both. These conclusions have been drawn previously (2).

The five Hawaiian rock samples are from the Waianae Volcano on the island of Oahu. Samples 6, 11, and 20 are from the lower member of this volcano [as described by MacDonald (10)] and were probably produced during a single stage of magmatic activity. Samples 31 and 178 are from the upper member of this volcano, and may not be as closely related to the former, more basic rocks. Nonetheless, it appears of some interest to consider all these rocks to be related and to attempt to define the behavior of Ga, Ge, and In during the course of magmatic activity. The five samples were chosen to form a suite of related rocks, extending from the most mafic sample, C-6, in order of increasing sample number to the most felsic sample, C-178. To observe possible trends through this suite, we plotted our data against the crystallization index defined by Poldervaart and Parker (11) (Fig. 1).

Gallium shows a pronounced enrichment during the course of magmatic fractionation [in disagreement with the data summarized by Prinz (3)]. Indium also appears to be enriched, although the C-31 point falls off a smooth curve fitted through the other points. The concentration of Ge does not appear to change appreciably during the fractionation process. Also shown are the concentrations of  $Na_2O$  and  $TiQ_2$  in the same rocks as reported by MacDonald and Katsura (10). These are also enriched in the later differentiates, TiO<sub>2</sub> to about the same degree as Ga and In, and  $Na_2O$ to a still greater extent.

One of the intriguing problems regarding the Mare Tranquillitatis samples

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is their high TiO<sub>2</sub> content. The most plausible explanations of this observation are that the enrichment is the result of a high-temperature volatilization or partial condensation process or the result of magmatic fractionation, or some combination of these possibilities. If volatility is the major cause of the enrichment, one would expect a negative correlation between the contents of TiO<sub>2</sub> and of In, which forms relatively volatile compounds. If magmatic fractionation has established the trends in the lunar samples, our preliminary data indicate that a positive correlation between In and TiO<sub>2</sub> would result. We will search for evidence regarding these possibilities in the data to be published from these proceedings.

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## Multielement Analysis of Lunar Soil and Rocks

Abstract. Results for multielement analysis of lunar soil and of seven rocks returned by Apollo 11 are presented. Sixty-six elements were determined with spark source mass spectrography and neutron activation. U.S. Geological Survey standard W-1 was used as a comparative standard. Results indicate an apparent uniformity of composition among the samples. Comparison with solar, meteoritic, and terrestrial abundances reveals depletion of volatile elements and enrichment of the rare earths titanium, zirconium, yttrium, and hafnium. Although there is an overall similarity of the lunar material to basaltic achondrites and basalts, the differences suggest detailed geochemical processes special to the history of this material.

Chemical analyses of lunar soil and seven rocks from the Apollo 11 mission were performed with spark source mass spectrography (MS) and neutron activation analysis (NAA); this resulted in the determination of approximately 66 elements per sample. Both methods as used for terrestrial samples have previously been described (1). The U.S. Geological Survey standard diabase W-1 was again used as a multielement standard, and the same literature values were employed.

For the lunar analyses, a few changes have been made in these methods. One gram of each sample was crushed; then 200 mg was removed for NAA, and 500 mg was removed for MS. For the shorter irradiations in NAA, flux and irradiation times were changed to compensate for the smaller sample size. For the longer irradiations, the samples were inserted in the central thimble of the TRIGA reactor with a resultant flux of  $3.5 \times 10^{12}$  neutron/cm<sup>2</sup>-sec. In the case

of MS, the 500-mg samples were mixed with equal amounts of graphite (National Carbon Co. spectroscopic powder). Because of small sample size, accurate doping of an internal standard for MS was not possible. Zirconium present in the samples represented a suitable internal standard, and the NAA determination for this element was used in the MS calculations.

Results of the analysis of the eight lunar samples received at our laboratory are given in Table 1, along with the method employed. Results from the method having the better accuracy (as determined by past analyses of terrestrial and meteoritic materials) and the better analytical conditions (higher sensitivity, lower background, and so forth) were used. When these criteria were judged equivalent, an arithmetic average of the results of the two methods was reported. Since these multielement methods possess variations in precision for each element, only average values