The significance of $CI/P_2O_5$ ratios.

In contrast to most trace element ratios, $CI/P_2O_5$ ratios of lunar rocks and soils are reported to cluster into three distinct populations. The lunar samples occurring in these groups are interpreted to have been derived from discrete volumes of differentiating magma. Indeed, supposed groupings based on $CI/P_2O_5$ ratios have been correlated with large convection cells and moon-wide accretional heterogeneities (1, 2, 3). However, before any further considerations of $CI/P_2O_5$ ratios are made, it is important to consider exactly where the $CI$ and $P$ reside within the lunar samples. The $CI$ in the sample used in this ratio is the "residual" $CI$, that is, $CI$ remaining after a 10 minute hot-water leach that is thought to remove all vapor-deposited $CI$. All the residual $CI$ "must have been present in some single chemical phase" (2) which, together with the $P$, is considered to occur in apatite and whitlockite. In this paper, we shall address the actual sites of $CI$ and $P$ in the lunar rocks, the $CI/P_2O_5$ ratios for these samples, and evaluate the significance of such data from both chemical and petrological viewpoints.

**CI-Bearing Phases**

There are several phases in the lunar rocks which have $CI$ as either a major or minor component. Two $CI$-bearing Zn-Fe sulfates have been reported from 66095, Rusty Rock, as occurring along cracks and grain boundaries and associated with lawrencite, $FeCl_2$, and possibly $ZnCl_2$ (5). These are the phases which are considered to be leached by the hot-water treatment, before the residual $Cl_r$ analyses are performed. The leachable phases are supposedly deposited by vapor and are not considered as primary. As discussed by Garrison and Taylor (6), the $CI$ and some of the $P$ from apatite may be mobilized by metamorphism and thereby migrate until they are picked up by a scavenger phase, namely FeNi metal. These elements react to form $FeCl_2$, lawrencite, and $(Fe,Ni)_3P$, schreibersite, resp., a model supported by the experiments of Cirrin and Housley (7). The amount of leachable $CI$, hence residual $CI$, may simply be a reflection of the amount of $CI$ released during impact-induced metamorphism (6).

It is the deliquescent $CI$-bearing phase lawrencite, $FeCl_2$, which oxyhydrates to $FeOOH$ (akaganeite) upon contamination with terrestrial water vapor (8). Some of the $Cl$ from the lawrencite is partitioned into the akaganeite. Typical analyses of the $FeOOH$ phase show 1-6% $Cl$ (5,9). This phase is not soluble in hot water and therefore, can contribute to the residual $Cl_r$ analyses. In fact, because "rust" (akaganeite) is present in the majority of all Apollo 16 rocks (Hunter & Taylor, this Vol.) and apatite is very rare, it is the $Cl$ in rust, $FeOOH$, which largely controls $Cl_r/P_2O_5$ ratios. That is, for Apollo 16 samples,

$$Cl^{r}_{FeOOH} \gg Cl^{r}_{apatite}$$

$$Cl^{r} = f(\text{lawrencite + apatite}) = f(\text{oxyhydration}) = f(\text{contamination})$$

The amount of $FeOOH$ phase present is a function of the degree of contamination by water vapor. Apollo 16 lunar samples have been exposed to various degrees of such contaminations in the "dry" $N_2$ glove boxes of the curatorial facilities. The only requirements for the $N_2$ purity of these boxes are that the $N_2$ contain less than 50 ppm $H_2O$ and less than 20 ppm $O_2$, more than enough vapor to oxyhydrate $FeCl_2$. Thus, the $Cl_r$ in such samples would appear to be largely a function of postlunar processes, in addition to the impact-induced metamorphism.

**P-Bearing Phases**

The major sources of $P$ in lunar samples are considered to be apatite, $Ca_5(P_0_{4})_2(Fe,Cl)$, and whitlockite, $Ca_3(P_0_{4})_2$. Jovanovic and Reed (1) consider one third of the $P_2O_5$ from the sample analyses to come from apatite, the
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remainder from whitlockite. However, for many rocks, including most highland samples, this is not the case.

The majority of the Apollo 16 rocks over 5 gms. contain schreibersite, (Fe,Ni)3P (15% P = 34% P2O5) and only rarely apatite (Hunter & Taylor, this Vol.). This phosphide mineral is commonly misidentified as troilite and usually occurs intergrown with native FeNi where it is not readily discernable to the unsuspicious eye. Native FeNi is an ubiquitous phase in lunar rocks. Besides the major components Fe, Ni, and Co, the native metal contains 0.02 to 1.53% P (equivalent to 3.5% P2O5) in solid solution. The amounts of FeNi metal grains and schreibersite in lunar samples are usually much greater than the contents of apatite and whitlockite, particularly in Apollo 16 rocks. To correlate P2O5 values solely with phosphate phases, therefore, is extremely misleading. Indeed, the native FeNi and schreibersite are probably the source of the major portion of the "P2O5" analyzed. That is:

\[ p_{\text{FeNi}} + p_{\text{schreibersite}} > p_{\text{apatite}} + p_{\text{whitlockite}} \]

CI/P2O5 Ratios Various elemental ratios have been used to model magmatic differentiation, but CI/P2O5 is an unlikely couple to use from petrological and geochemical considerations. Is the CI/P2O5 ratio of a rock or an apatite diagnostic of the primary magma? Jovanovic and Reed (2) report three major groups of CI/P2O5 ratios which they claim are distinct: 0.004, 0.009, and 0.021. These are attributed to variations in CI/P2O5 ratios in each of three distinct volumes of magma. Is this realistic? In one of the samples analyzed (10044), the whole-rock ratio is 0.007 while that of the apatite in this sample is 0.001 (10). This would seem to indicate the necessity for another CI-bearing phase, perhaps rust. In fact, the CI/P2O5 of numerous analyzed lunarapatites varies from 0.001 to 0.046 (11) twice their value for the 0.021 group.

Brown and Peckett (12) presented analyses of apatites from the Skaergaard Intrusive Complex. Using their data, calculation of CI/P2O5 indicates that this ratio varies by over an order of magnitude in the apatites, more than twice the 0.004, 0.009, and 0.021 groups of Jovanovic and Reed (2). One differentiated magma could easily account for all of the "groups".

CI/P2O5 "Groups"?? Using the tables of Clr and P2O5 analyses from Jovanovic and Reed (2), Figures 1 and 2 were constructed. Lunar breccias and soils have significant meteoritic contributions; in light of the above mineralogic complications, data from these types of samples are of questionable significance for Clr and P2O5. As can be seen on Figure 1, most of the data points are from these types of samples. In fact, all of the data points outside of the main cluster are from soils and breccias. If these outer points are discarded, or even if they are not, from whence cometh the three populations??

In conclusion, we find no redeeming factor(s) for consideration of Clr/P2O5 ratios for lunar samples. No apparent significance can be placed on these data.
