the single species model has opened one avenue for delving into community and ecosystem problems through the modeling approach of systems analysis.

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1 June 1971; revised 27 September 1971 ■

Crystallization Studies of Lunar Igneous Rocks: Crystal Structure of Synthetic Armalcolite

Abstract. *Crystals of armalcolite, $Mg_{0.5}Fe_{0.5}Ti_2O_5$, up to several millimeters in length have been grown from a glass initially having the composition of lunar rock 10017. A single-crystal x-ray study has confirmed that the crystals are isomorphous with pseudobrookite and has shown that the cations are strongly ordered, with the Ti^{4+} ions occupying the* 8f *sites and the Fe^{2+} and Mg^{2+} ions randomly distributed over the* 4c *sites. An examination of karrooite, $MgTi_2O_5$, has revealed a similar distribution of Mg^{2+} and Ti^{4+} ions. A reexamination of earlier x-ray and Mössbauer data for pseudobrookite, Fe_2TiO_5, has shown that it is more consistent with this type of ordering than with the inverse structure that has been generally assumed.*

During an investigation of the feasibility of studying the crystallization of lunar igneous rocks by high-temperature x-ray diffractometer techniques, we have obtained black needle-like crystals that have proved to be the mineral armalcolite, $Mg_{0.5}Fe_{0.5}Ti_2O_5$, recently discovered in the Apollo 11 lunar samples (*1*). Many of these crystals are several millimeters long and several tenths of a millimeter in cross section and lie in the surface of the solidified melt; thus, sections can be removed that are ideal for investigation of the structure by single-crystal x-ray techniques. We have also grown and studied crystals of the isomorphous mineral karrooite, $MgTi_2O_5$. We have found that the distribution of cations in these crystals is the inverse of that proposed for the isomorphous mineral pseudobrookite, Fe_2TiO_5 (*2, 3*). A reconsideration of x-ray (*2, 3*) and Mössbauer (*4*) data on pseudobrookite has led us to conclude that the previously proposed cation arrangement is probably incorrect.

The starting material for our crystallization studies, a glass corresponding closely in composition to lunar rock 10017 (*5*), was prepared from pure oxides, Fe metal, and synthetic anorthite ground together and pressed into pellets. The mixture was melted with an induction furnace in a closed Fe crucible in an Ar atmosphere, and after several hours above the liquidus temperature was "quenched" by turning off the power. Microscopic examination showed occasional small octahedrons of metallic Fe to be the only crystalline phase present.

Four experiments at high temperature were made in a Materials Research model X-86-G2 furnace; the powder x-ray diffractometer was General Electric model XRD-5. In each experiment a few milligrams of powdered glass (particle size less than 44 μm) in an acetone slurry was put on the heater strip of the furnace. In one experiment a heater made of Pt with 40 percent Rh was used and the sample volume was continuously pumped to maintain a total pressure of about 10^{-5} mm of Hg. In the other experiments Mo strips were used, in one case pumped as above, then with flowing He at 10^{-4} mm of Hg, and finally with flowing H_2 at 10^{-3} mm of Hg. In each case the temperature of the heater was raised until the sample spread over the strip as a smooth film and then lowered in steps of about 25°C. At each temperature the x-ray powder pattern was recorded with MoKα radiation. In all cases armalcolite was the first phase to crystallize, and it remained stable as the temperature was gradually lowered to about 1000°C, at which point the sample was fairly rapidly cooled to room temperature. No ilmenite formed during these experiments.

In lunar rock 10017 ilmenite is abundant while no armalcolite is found. The same is true of the synthetic 10017 melt when it is cooled in an Fe crucible in an inert atmosphere. In the case of the experiment on Pt–(40 percent)-Rh, loss of Fe from the melt was evidenced by bubbling and the formation of a clear glass layer next to the strip. Although it was expected that loss of Fe would be less severe on the Mo strips (*6*), and such obvious evidence of loss was not seen there, the

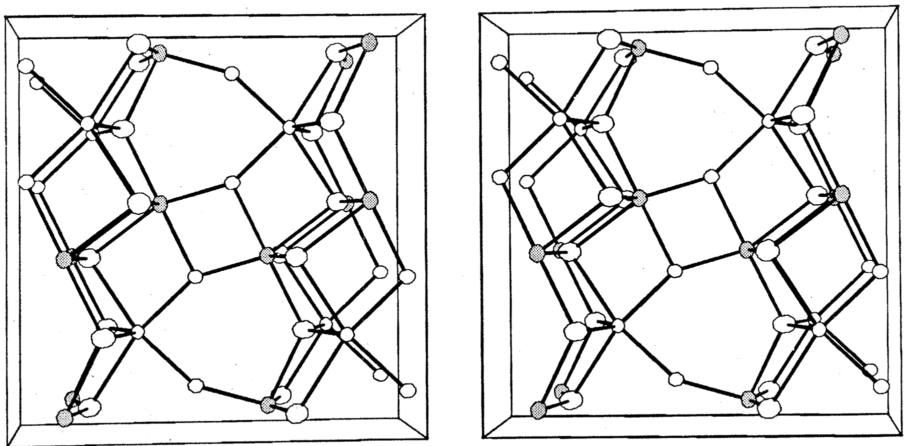

Fig. 1. Stereoscopic view of the contents of one unit cell of armalcolite. The viewing direction is along the *c* axis. The cations in 8*f* sites are shaded. The ellipsoids indicating the thermal motion probability are scaled to include 75 percent probability.

Table 1. Crystal data.

Quantity	Armalcolite ($Fe_{0.5}Mg_{0.5}Ti_2O_5$)	Karrooite ($MgTi_2O_5$)
Space group	*Bbmm*	*Bbmm*
a axis	9.76 ± 0.02 Å	9.75 ± 0.02 Å
b axis	10.01 ± 0.02 Å	10.00 ± 0.02 Å
c axis	3.74 ± 0.01 Å	3.75 ± 0.01 Å
Unit cell volume, *V*	365.4 $Å^3$	365.6 $Å^3$
Formula units per unit cell	4	4
Formula weight	215.0	200.1
Calculated density, d_{calc}	3.92 g cm^{-3}	3.63 g cm^{-3}
Linear absorption coefficient, $\mu_{MoK\alpha}$	64.4 cm^{-1}	45.8 cm^{-1}

simplest explanation of the results is that Fe loss from the melt with the subsequent formation of armalcolite occurred in all cases. The armalcolite crystals grew as needles in the plane of the strip heater with their *a* axes strongly oriented normal to the plane, which greatly enhanced the intensity of the 200 and 400 reflections.

The karrooite crystals were obtained by melting a 1:2 mixture of MgO and TiO_2 in an Ir crucible in air with an induction furnace and annealing at about 1500°C for 12 hours.

The most probable space group and the lattice constants were determined from Buerger precession photographs taken at room temperature, 23°C. These and related crystallographic data are given in Table 1.

The x-ray diffraction intensity data were measured with a Buerger-Supper-Pace-Picker automatic diffractometer, MoKα radiation, and balanced Zr and Y filters. The crystals were rotated around the *c* axis. The continuous scan mode was used, with a scan rate of 1 deg per minute, a scan interval of 2 deg and upward, and background counts of 20 seconds and upward at the beginning and at the end of the scan interval. All the independent intensities $I(hkl)$ with $(\sin\theta)/\lambda \leqslant 0.65$ Å^{-1}, a total of 255, were measured for each crystal. The crystals used for the intensity measurements were rectangular plates of the following dimensions: armalcolite, 0.018 by 0.049 by 0.208 mm^3 and karrooite, 0.061 by 0.085 by 0.244 mm^3; the dimensions are along axes *a*, *b*, and *c*, in that order. The intensities were corrected for absorption by the method of Burnham (*7*), the correction factors being between 1.12 and 1.36 for armalcolite and between 1.31 and 1.47 for karrooite. The intensities were reduced to relative values of $|F_o(hkl)|^2$, where F_o is the observed structure factor, by application of the appropriate Lorentz-polarization and Tunell factors.

The structural parameters were refined by the method of least squares with the computer program Orfls (*8*). The scattering factors used were those for Fe^{2+}, Mg^{2+}, and Ti^{4+} given by Cromer and Waber (*9, 10*), and those for O^{2-} given by Tokonami (*11*). The real parts of Cromer's anomalous dispersion corrections were applied to the scattering factors of the cations. Weights *W* were assigned to the $|F_o(hkl)|$ by a modification of the Hughes procedure: for $|F_o(hkl)| \geq 20$, $W = 400/|F_o(hkl)|^2$ and for $|F_o(hkl)| < 20$, $W = 1$. The refinement calculations converged to the parameter values given in Table 2. The final values of the agreement index $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ were 0.023 and 0.022 for the armalcolite and the karrooite, respectively. The observed structure amplitudes and those calculated from the final parameter values have been tabulated for armalcolite and karrooite (*12*).

As expected, the arrangement of the oxide ions in both crystals is very nearly the same as that reported for pseudobrookite (*2, 3*). However, our results indicate a quite different distribution of cations. We determined the distribution of cations between the two cation sites, 4*c* and 8*f* of space group *Bbmm* (see Table 2), by letting the site occupancy factors be least-squares variables which adjusted the contribution of each cation in each site, subject to the constraint that the occupancy factors add to 4 and 8 as required by the space group.

For armalcolite our results indicate that essentially all the Ti^{4+} ions are in the 8*f* sites and that the 4*c* sites contain Fe^{2+} and Mg^{2+} in a ratio very close to 1. It is important to note that

Table 2. Final parameter values. The estimated standard errors as calculated by the least-squares program are given in parentheses.

Atom	Position*	Occupancy	10^5x	10^5y	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{13}$
				Armalcolite				
Fe Mg	4*c*	2.016(33) 1.984	80752(9)	¼	136(14)	142(13)	1273(98)	0
Ti	8*f*	8†	13486(6)	43549(7)	170(12)	202(10)	1344(90)	−34(29)
O(1)	4*c*	4	22662(44)	¼	395(45)	247(41)	1714(276)	0
O(2)	8*f*	8	4690(24)	88488(32)	174(30)	136(23)	1772(265)	14(94)
O(3)	8*f*	8	31306(29)	93462(31)	371(45)	249(27)	1666(307)	−359(127)
				Karrooite				
Mg Ti	4*c*	2.741(26) 1.259	80697(8)	¼	122(12)	141(12)	1129(79)	0
Ti Mg	8*f*	6.741 1.259	13495(4)	43580(4)	127(11)	157(9)	994(78)	33(22)
O(1)	4*c*	4	22912(24)	¼	284(21)	116(25)	1384(149)	0
O(2)	8*f*	8	4622(15)	88483(17)	181(17)	119(17)	1900(154)	−6(52)
O(3)	8*f*	8	31195(18)	93338(15)	164(28)	190(20)	364(189)	159(70)

* Positions 4*c* are: $x,¼,0$; $\bar{x},¾,0$; $½+x,¼,½$; $½-x,¾,½$. Positions 8*f* are: $x,y,0$; $\bar{x},\bar{y},0$; $x,½-y,0$; $\bar{x},½+y,0$; $½+x,y,½$; $½-x,\bar{y},½$; $½+x,½-y,½$; $½-x,½+y,½$. † See discussion of cation distribution in text.

the mean values of the scattering factors of the Fe^{2+} and Mg^{2+} ions are only slightly smaller than the scattering factors of the Ti^{4+} ions, which causes considerable difficulty in distinguishing the ions in the two sites. When the occupancy factors for the 8*f* and the 4*c* sites were allowed to vary simultaneously, the 8*f* sites appeared to be filled with Ti^{4+}, but the limits of error, as must be expected, were rather large (about 15 percent). The limits of error given in Table 2 for the occupancy factors of the Fe^{2+} and Mg^{2+} ions were obtained with the occupancy factor of the Ti^{4+} ions held constant.

Because of the aforementioned difficulty, we also decided to study the karrooite crystals. From Table 2 it can be seen that the positional and thermal parameters of the two crystals differ only slightly. Our results for karrooite indicate that the 8*f* sites are 84.2 ± 0.6 percent occupied by Ti^{4+} ions and 15.8 ± 0.6 percent by Mg^{2+} ions, while the 4*c* sites contain 68.4 ± 1.2 percent Mg^{2+} ions and 31.6 ± 1.2 percent Ti^{4+} ions. These limits of error are much lower than those for armalcolite. This result for karrooite reinforces our conclusion that in armalcolite essentially all the Ti^{4+} ions are in the 8*f* sites.

The limits of error in the occupancy factors for armalcolite are large enough that a distribution of Ti^{4+} ions similar to that in karrooite cannot be ruled out. On the other hand, since the crystals of karrooite were annealed at a considerably higher temperature than those of armalcolite, the Ti^{4+} ions may be more highly ordered on the 8*f* sites in armalcolite.

Mössbauer spectra, which have been obtained at room temperature for material removed from the Pt–(40 percent)-RH heater strip, show in addition to absorption due to Fe^{2+} in glass, a sharp doublet of Fe^{2+} in armalcolite. This sample was subjected to the most oxidizing conditions of the series of crystallization experiments. The data are consistent with no Fe^{3+} in the armalcolite and place an upper limit of about 0.2 on the fraction of the Fe in the armalcolite that could be Fe^{3+}. The single, sharp doublet also indicates that most of the Fe^{2+} is in crystallographically equivalent sites. This is even more strongly implied by the sharp magnetic hyperfine pattern obtained from $FeTi_2O_5$ at low temperatures by Muranaka *et al.* (*4*).

Previous workers assumed that in pseudobrookite, Fe_2TiO_5, the eight Fe^{3+} ions per unit cell are in the 8*f* sites and the four Ti^{4+} ions are in the 4*c* sites. Because our results indicate that the Ti^{4+} ions prefer the 8*f* sites in this structure, we reexamined the published x-ray diffraction and Mössbauer spectroscopic data for pseudobrookite. By a least-squares refinement of the pseudobrookite parameters from Hamelin's x-ray diffraction data (*2*), we found that considerable improvement in the agreement between $|F_o(hkl)|$ and $|F_c(hkl)|$ can be obtained if it is assumed that there are four Fe^{3+} ions in the 4*c* sites, with the 8*f* sites occupied by the remaining four Fe^{3+} ions and the four Ti^{4+} ions. This distribution is supported by the Mössbauer spectrum (*4*) of pseudobrookite, which is that expected for nearly equal numbers of Fe^{3+} ions in two crystallographically nonequivalent sites.

The armalcolite structure is illustrated in Figs. 1 and 2, both of which were drawn with the computer program Ortep (*13*). Some interionic distances of interest, calculated by the computer program Orffe (*14*), are indicated in Fig. 2. The values given in the figure are for armalcolite. Those for karrooite differ by no more than 0.01 Å except for the longest distance shown, which is 0.02 Å shorter. The limits of error in these distances are 0.015 Å (three times the estimated standard errors calculated by the computer program).

There is octahedral coordination of oxide ions around each cation in the structure. Four of the six oxide ions bonded to each cation approach the cation more closely than the other two. The four more closely held oxide ions form an irregular tetrahedron around each cation, and are joined by the two less tightly bonded oxide ions to form an irregular octahedron.

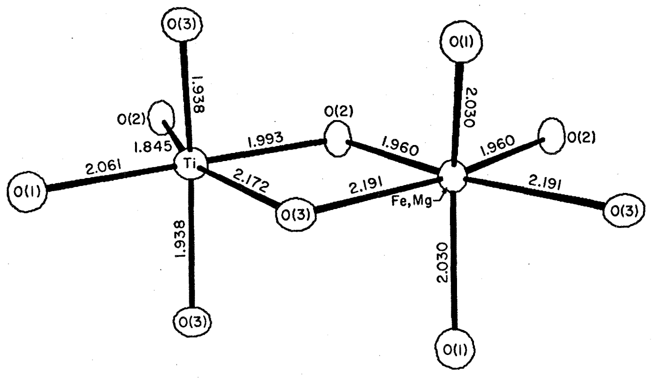

Fig. 2. View in perspective showing the environments of the two cation sites in armalcolite. The ellipsoids indicating the thermal motion probability are scaled to include 75 percent probability.

The Ti^{4+}–O^{2-} distances are, on the average, about 0.07 Å shorter than the $(Fe,Mg)^{2+}$–O^{2-} distances. This adds support to our conclusion that the structure is ordered with respect to the Ti^{4+} ions. Substantial disorder of the Ti^{4+} ions would probably cause the cation–oxide ion distances in the 8*f* and 4*c* sites to appear more nearly equal.

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15. We thank D. H. Hengstenberg for valuable technical assistance and M. L. Blander for advice in preparation of the synthetic rock glass. Partially supported by NASA contract NAS9-11539.

23 September 1971