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LUNAR TRIDYMITE AND CRISTOBALITE

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Abstract

Tridymite and cristobalite in lunar basalt 15085 are better than 99% SiO_2; they contain small percentages of TiO_2 (0.38, 0.28), Al_2O_3 (0.18, 0.34), K_2O (0.17, 0.26), and Na_2O (0.05, 0.05). The approximate equivalence of Al to K + Na indicates substitution of the type KAl = Si, the large cations being accommodated in lattice vacancies.

One of the mineralogical surprises in the Apollo 11 rocks returned to Earth was the rather frequent occurrence of tridymite and cristobalite as accessory minerals. This feature has been repeated in the rocks from later missions. Typically the tridymite occurs as thin platy crystals (appearing as narrow laths in thin sections), and the cristobalite as anhedral to subhedral grains (Figs. 1 and 2). The cristobalite shows a mosaic structure with a rectangular blocky appearance and low birefringence, attributed to inversion from the high–temperature form. The tridymite also shows patchy extinction attributable to inversion from the high–temperature form; it also has low birefringence (0.003 approx.) but somewhat higher than the cristobalite (0.001 approx.).

Rock 15085, a pyroxene–plagioclase basalt from the Mare Imbrium surface near the Apollo 15 landing site, contains well–developed tridymite (0.7 percent by weight) and cristobalite (0.4 percent). The comparatively coarse grain–size made these minerals particularly suitable for microprobe analysis, which was carried out with a view

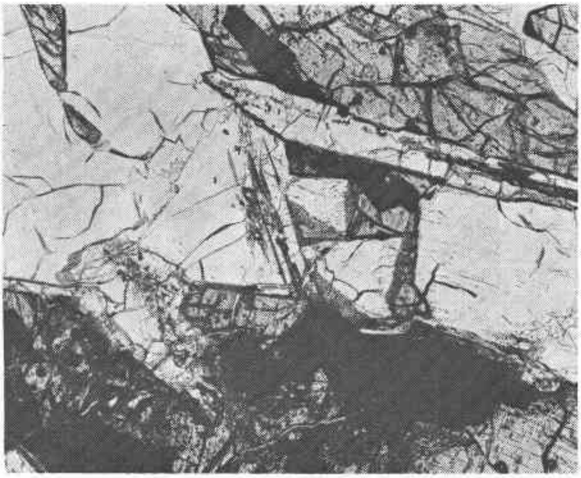

FIG. 1. Tridymite crystal, 1.5 × 0.1 mm, associated with anorthite (white) and augite (gray), in lunar rock 15085 (Smithsonian Institution photograph).

to determining how close the compositions were to pure SiO_2, and whether these two polymorphs showed distinctive differences in minor element contents. For comparison, analyses were also made of tridymite from the Haraiya eucrite and the Mt. Padbury mesosiderite, two meteorites whose silicate material is comparable in composition

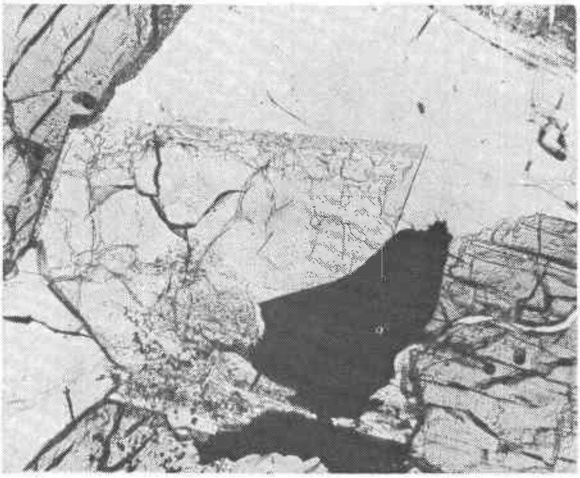

FIG. 2. Subhedral cristobalite, 0.6 mm across, in lunar rock 15085 (Smithsonian Institution photograph).

Table 1. Analyses of tridymite and cristobalite; bracketed SiO_2 values are by difference. Ba and Sr were looked for in analyses 1-4 but not found, i. e. < 0.02%.

	1	2	3	4	5
SiO_2	[99.13]	[99.05]	[99.77]	[99.52]	99.47
TiO_2	0.38	0.28	0.03	0.07	none
Al_2O_3	0.18	0.34	0.14	0.21	0.17
FeO	0.09	<0.02	<0.02	0.06	0.03
MnO	<0.02	<0.02	<0.02	<0.02	none
MgO	<0.03	<0.03	<0.03	<0.03	trace
CaO	<0.02	0.02	0.05	0.08	trace
Na_2O	0.05	0.05	<0.04	<0.04	0.12
K_2O	0.17	0.26	0.04	0.06	0.01
P_2O_5	<0.03	<0.03	<0.03	<0.03	none

1. Cristobalite, 15085.
2. Tridymite, 15085.
3. Tridymite, Mt Padbury mesosiderite.
4. Tridymite, Haraiya eucrite.
5. Tridymite, Steinbach meteorite (Grant, 1967).

to the lunar basalts. The results are given in Table 1, along with the published analysis of tridymite from the Steinbach meteorite, a unique type consisting of nickel–iron, orthopyroxene (Fs_{15}), and tridymite.

The first noteworthy feature of the lunar minerals is their close approach to pure SiO_2; not so close, however, as the meteoritic tridymites. The difference is partly, but not entirely, due to the presence of appreciable TiO_2 in the lunar minerals, presumably caused by their crystallization from a medium relatively rich in titanium (the lunar rock 15085 contains 3.07 percent TiO_2, the Mt. Padbury meteorite 0.30 percent, and the Haraiya meteorite 0.57 percent).

A second significant feature in all the analyses in Table 1 is the close approach of the molecular ratio of Al_2O_3 to ($Na_2O + K_2O + CaO$) to unity. This indicates that the replacement is of the type K + Al = Si, the large Na, K, and Ca ions being accommodated in vacancies in the tridymite and cristobalite structures (one may recall the close structural relationship between high–tridymite and nepheline). The possibility of the replacement AlP = 2Si was envisaged, so phosphorus was looked for with the microprobe, but none was found. The low calcium content is intriguing, in view of the association of the lunar tridymite and cristobalite with anorthite and calcic pyroxene. This may reflect a low calcium concentration in the magma after much of the anorthite and pyroxene has crystallized, or possibly ionic size and/or valency militate against the acceptance of this element into the structures of tridymite and cristobalite. The practical absence of iron, manganese, and magnesium indicates that these elements are not readily accommodated in these minerals. The predominance of potassium over sodium in this lunar tridymite and cristobalite may be due to a relatively high K/Na ratio in the late magmatic liquid.

There appear to be no significant compositional differences between the two polymorphs in 15085, except perhaps a somewhat lower K_2O and Al_2O_3 content in the cristobalite. Brown *et al.* (1970) analysed coexisting tridymite and cristobalite in lunar rock 10017 and found the tridymite differed from the cristobalite in containing appreciable K_2O (0.17%) but no detectable Na_2O. Klein *et al.* (1971) analysed these two polymorphs in lunar gabbro 12064 and record 0.25 percent K_2O in the tridymite and 0.0 percent in the cristobalite. There is thus some indication for preferential concentration of potassium in tridymite, but additional data are needed to confirm this.

A considerable number of analyses of lunar tridymite and cristobalite have been published (far more, incidentally, than of terrestrial occurrences of these minerals). The most extensive series has been provided by Busche *et al.* (1971), who published 29 analyses of silica minerals (polymorph not specified) in Apollo 12 samples. Their results are as follows (range and average): SiO_2 96.2–98.4, 97.1; Al_2O_3 0.39–1.40, 0.74; FeO 0.09–1.06, 0.47; CaO 0.03–0.72, 0.45; Na_2O 0.02–0.18, 0.12; K_2O 0.01–0.25, 0.05. The summations of their analyses are mostly somewhat less than 100.00, probably in part because TiO_2 was not determined. In general, their analyses show consistently lower SiO_2 contents than those in Table 1, and a poorer balance between Al_2O_3 and $CaO + Na_2O + K_2O$; the relatively high FeO contents are noteworthy. A useful check on this apparent variability in composition could be readily obtained if refractive index data were available. According to Grant (1967) the indices for pure synthetic tridymite are $\alpha = 1.471$, $\beta = 1.472$, $\gamma = 1.474$, and they increase with increasing content of foreign elements. For tridymite in 15085 I found $\alpha = 1.472$, $\gamma = 1.475$, and identical figures for this mineral in 15271, 15471, and 15475. For cristobalite in 15085 I found $n = 1.487$, birefringence $\approx$ 0.001, and the same value for cristobalite in 15475. Within my very limited sampling it appears that the compositional variation of lunar tridymite and cristobalite may be quite small.

Some X-ray data have been published on lunar tridymite and cristobalite. The most precise cell dimensions appear to be those of Appleman *et al.* (1971); they found that cristobalite from three Apollo 12 rocks is tetragonal, with $a = 4.978–4.981$ Å, $c = 6.931–6.937$ Å, and a cell volume ranging from 171.8 to 172.1 Å^3; tridymite from rock 12021 is apparently orthorhombic, with $a = 8.600$ Å, $b = 4.999$ Å, $c = 8.205$ Å, and cell volume 355.2 Å^3.

The presence of both tridymite and cristobalite in 15085 and many other lunar rocks provides some evidence of conditions of crystallization. The textural relationship between tridymite, plagioclase, and pyroxene in 15085 suggests that silicate crystallization began with pyroxene, followed by plagioclase, with tridymite coming in at a late stage and crystallizing together with the other minerals. Huebner and Ross (1972), in a study of lunar pyroxenes, give a tentative liquidus diagram for the pyroxene quadrilateral which shows a eutectic in the iron-rich region at a temperature just below 1000°C, yielding the subsolidus assemblage augite + olivine + silica + orthopyroxene or pigeonite. At this temperature the thermodynamically stable form of silica is tridymite, and this assemblage, with the addition of anorthite, corresponds fairly closely to the actual assemblage in 15085. This indicates that the temperature of complete crystallization of this rock was about 1000°C or somewhat less. The cristobalite, however, clearly crystallized outside its thermodynamic stability field, which is at 1470°C or higher. The cristobalite was not observed in contact with tridymite, and there is no direct evidence that they crystallized simultaneously. The cristobalite occurs as irregular patches interstitial to the major minerals of the rock, and appears to be late in the crystallization sequence, possibly even later than tridymite. The conditions favoring the formation of cristobalite over tridymite must be primarily kinetic, presumably related to ease of nucleation. Possibly the cristobalite was formed during rapid cooling of the rock during the final stages of crystallization. However, too rapid cooling probably resulted in the formation of silica-rich glass rather than the crystallization of cristobalite. My observations indicate that cristobalite is found predominantly in the coarser-grained rocks, whereas in the finer-grained rocks the residual magmatic liquid congealed as a glass.

At first glance it is remarkable that the lunar tridymite and cristobalite, in rocks which crystallized more than three billion years ago, have not inverted to quartz, as has occurred in most ancient terrestrial rocks. Tridymite and cristobalite have also survived in meteorites, for which crystallization ages of about 4.6 billion years have been established. The survival of these high-temperature polymorphs in meteorites and lunar rocks can probably be ascribed to the extremely anhydrous nature of these materials; the catalytic action of water in promoting recrystallization and equilibration is well documented.

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FLUORESCENT HYDROGROSSULAR FROM NORDLAND, NORWAY.

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ABSTRACT

Fluorescent hydrogrossular is reported from a vesuvianite-bearing marble from near Mosjøen, North Norway, and the modes of occurrence of the mineral are described. In the same rock non-fluorescent grossular is present in the narrow contact zone of two monzonitic dikes. The hydrogrossular formed during the second of two main crystallization episodes, probably by metasomatism asso-