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Aluminum-Titanium-Rich Pyroxenes, with Special Reference to the Allende Meteorite

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Abstract

Some chondrules in the Allende Type III carbonaceous chondrite contain the assemblage spinel-melilite-clinopyroxene. The clinopyroxene has high Ti and Al contents unmatched in terrestrial, lunar, and most meteoritic pyroxenes. It is an essentially pure CaMgAlTiSi compound, with only trace amounts of other elements. The principal components are TiO_2 (3.9–17.7 percent), SiO_2 (31.3–42.7 percent), Al_2O_3 (16.0–22.0 percent), and MgO (5.1–11.9 percent). In terms of atoms per 6 oxygens, Si is 1.16–1.57, Ti 0.11–0.49, Al 0.69–0.96, Mg 0.28–0.65; Ca is uniformly close to 1.00. In terms of pyroxene components, the Allende pyroxene is made up of $CaMgSi_2O_6$, $CaAl_2SiO_6$, $CaTiAl_2O_6$, and $CaTiAlSiO_6$; the latter component has Ti in the trivalent state and amounts to some 40 percent in the most Ti-rich compositions. There is evidence for a wide miscibility gap between these compositions and the field of fassaite in synthetic and natural pyroxenes.

Introduction

The mineralogical investigation of the Allende meteorite, a carbonaceous chondrite which fell in Mexico on February 8, 1969, has revealed the presence, in Ca- and Al-rich chondrules and aggregates, of pyroxenes with unusually high contents of Al_2O_3 and TiO_2 (Table 1). The only comparable Al,Ti-rich pyroxene known to occur in meteorites is in Vigarano, which is similar to Allende in composition (Michel-Levy, Caye, and Nelen, 1970). Other meteoritic pyroxenes are usually quite low in these elements, the only exception being a titanaugite with 2.3 percent TiO_2 and 9.6 percent Al_2O_3, which is the dominant mineral in the unique Angra dos Reis achondrite (Hutchison, 1972). Some lunar pyroxenes are relatively rich in these elements; a brief literature search gave maximum figures of 9.1 percent Al_2O_3 and 9.3 percent TiO_2 in a pyroxene in Apollo 11 microbreccia 10068 (Bunch, Keil, and Prinz, 1970).

Terrestrial Ti- and Al-rich pyroxenes are uncommon. The most extreme example I have found in the literature is a uniaxial titanaugite (14.29 percent Al_2O_3 and 5.72 percent TiO_2) in a sphene-rich plagioclase-diopside hornfels from Schivas, Aberdeenshire (Dixon and Kennedy, 1933). Aluminum-rich, titanium-poor pyroxenes are more common, *e.g.* in contact metamorphosed limestones and dolomites. Werner introduced the name fassaite into mineralogy for this type of pyroxene found in such rocks in the Val di Fassa (Italian Tyrol); numerous analyses have been published, all very similar, and averaging 10 percent Al_2O_3. The maximum Al_2O_3 reported in a terrestrial fassaite is 15.75 percent in one from Helena, Montana (Knopf and Lee, 1957), and Rao and Rao (1970) have described one with 12.43 percent from Orissa, India; however, TiO_2 is low in these (less than 1 percent).

From the original description and subsequent usage, the name fassaite should be used for a pyroxene with an appreciable content of the $CaAl_2SiO_6$ component, often referred to as "lime-Tschermak's molecule" and abbreviated as CTs or CaTs. High-aluminum pyroxenes, which are sometimes referred to as fassaites, occur as xenocrysts in alkali basalts, but these are low in calcium, and this aluminum component can be calculated as $MgAl_2SiO_6$, the magnesium equivalent of Tschermak's molecule.

Data from Synthetic Studies

The Allende pyroxenes (Table 1) have a rather simple composition with only five components; iron is notably absent or present only in trace amounts. If we neglect for the present the possible occurrence of titanium in the Ti^{3+} state, the analyses in Table 1 can be plotted in the three-component system

TABLE 1. Pyroxene Compositions in the Allende Meteorite*

	SiO_2	TiO_2	Al_2O_3	FeO	MgO	CaO	Reference
A	42.7	3.9	16.0	<0.1	11.9	25.9	Mason and Martin, 1974
B	39.5	5.2	20.1	0.1	10.5	24.5	Gray et al., 1973
C	39.8	5.5	18.2	<0.1	9.7	25.4	Clarke et al., 1970
D	37.2	9.2	18.3	0.0	9.4	24.6	Marvin et al., 1970
E	38.5	11.2	16.9	<0.1	9.4	24.3	Gray et al., 1973 .
F	32.8	16.6	19.3	<0.1	6.7	24.6	Dowty and Clark, 1973
G	33.5	16.9	17.3	0.03	7.7	24.1	Fuchs, 1971
H	32.8	17.3	18.3	<0.1	7.1	25.2	Gray et al., 1973
I	31.3	17.7	22.0	0.0	5.1	24.9	Fuchs, 1971

Atoms per 6 oxygens

	Si	Ti	Al	Mg	Ca	Sum
A	1.57	0.11	0.69	0.65	1.01	4.03
B	1.44	0.14	0.87	0.55	0.97	3.97
C	1.47	0.15	0.80	0.54	1.01	3.97
D	1.36	0.26	0.80	0.52	0.99	3.93
E	1.41	0.31	0.73	0.51	0.96	3.92
F	1.22	0.47	0.85	0.37	0.99	3.90
G	1.25	0.48	0.76	0.43	0.97	3.89
H	1.22	0.48	0.80	0.39	1.00	3.89
I	1.16	0.49	0.96	0.28	0.99	3.88

Refractive indices and unit-cell dimensions (A)

	α	β	γ	a	b	c	β	V
A	1.697	1.704	1.729					
C	1.705	1.713	1.735	9.725	8.828	5.306	105°55'	438.1A^3
F	1.747	1.750	1.763	9.80	8.85	5.36	105°37'	448.2A^3

*Dowty and Clark present evidence for their specimen containing Ti^{3+}, and report the total titanium as 10.7% Ti_2O_3 and 4.7% TiO_2.

$CaMgSi_2O_6$-$CaAl_2SiO_6$-$CaTiAl_2O_6$ (Fig. 1). This system has not been completely investigated, but considerable information is available for parts of it.

The $CaAl_2SiO_6$ pyroxene has a limited stability field above 1150°C and 10 kbar (Hays, 1967); below 10 kbar the stable assemblage for this composition is anorthite + gehlenite + corundum. De Neufville and Schairer (1962) studied the $CaMgSi_2O_6$-$CaAl_2SiO_6$ join at 1 atm, and found that $CaMgSi_2O_6$ can accommodate up to 20 wt percent $CaAl_2SiO_6$ in solid solution (equivalent to 9.4 percent Al_2O_3). At higher concentrations of $CaAl_2SiO_6$, this solid solution coexists with melilite solid solutions and anorthite; other phases, such as spinel, also appear. As the concentration of $CaAl_2SiO_6$ in the system was increased, the melilite solid solutions showed a regular change in composition, from essentially pure $Ca_2MgSi_2O_7$ (akermanite) at the 20 percent level to $Ca_2Al_2SiO_7$ (gehlenite) in compositions close to pure $CaAl_2SiO_6$.

The join $CaMgSi_2O_6$-$CaTiAl_2O_6$ was studied at 1 atm pressure by Yagi and Onuma (1967), who found a maximum solubility of 11 wt percent $CaTiAl_2O_6$ in diopside, equivalent to 3.7 percent TiO_2. Higher pressures diminish the solubility. The stable association for the composition $CaTiAl_2O_6$ is perovskite + corundum; spinel appears in place of corundum when Mg is available from the $CaMgSi_2O_6$ component.

Experimental studies of the incorporation of titanium in pyroxene were reported by Barth (1931) and Segnit (1953). Barth prepared homogeneous pyroxene of the composition 90 $CaMgSi_2O_6$ + 10 $CaMgTi_2O_6$ (equivalent to 6.2 percent TiO_2) by heating a mixture of the constituent oxides at 1300°C for two hours. Segnit studied the limits of solid solution of TiO_2 in $CaMgSi_2O_6$ by preparing glasses at 2 percent TiO_2 intervals along the diopside-oxide join to a limit of 10 percent oxide, and then crystallizing the glasses by heating them below their solidus temperatures. He found the limit for homogeneous

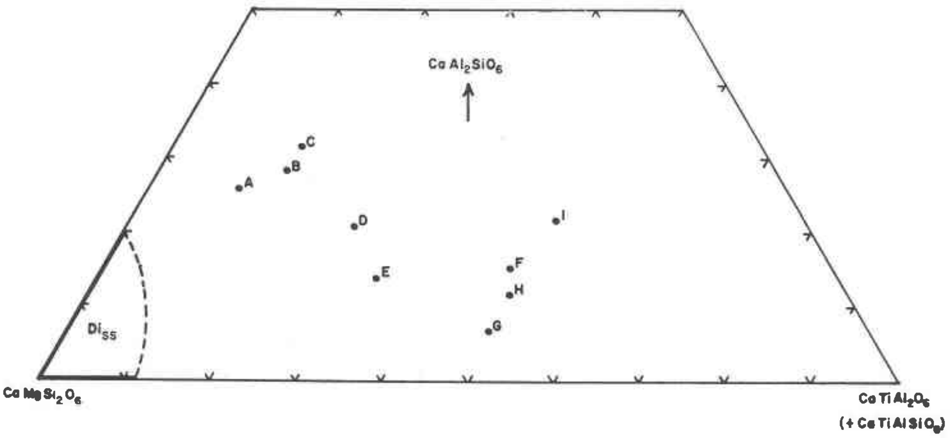

FIG. 1. Part of the system $CaMgSi_2O_6$-$CaAl_2SiO_6$-$CaTiAl_2O_6$+$CaTiAlSiO_6$, showing the relationship of the Allende pyroxene compositions (Table 1) to the field of diopside solid solutions at 1 atm pressure.

crystallization was 6 percent TiO_2. It is not certain, however, that the titanium-rich pyroxenes prepared by Barth and Segnit were true equilibrium products.

It appears that the compositions of terrestrial Ti- and Al-rich pyroxenes are generally consistent with the equilibrium concentrations indicated by synthesis. Fassaites with more than 20 percent of the $CaAl_2SiO_6$ component, the limit of miscibility at 1 atm pressure, are comparatively rare, and their geological occurrence suggests crystallization under higher pressures. The upper limit of TiO_2 in terrestrial pyroxenes appears to be about 6 percent, consistent with the data of Barth and Segnit but somewhat higher than the limit of 3.7 percent TiO_2 established by Yagi and Onuma for the $CaMgSi_2O_6$-$CaTiAl_2O_6$ join. Of course, the greater complexity of natural systems may increase the diadochy of Ti and Al in the crystallizing pyroxenes. In particular, a low SiO_2 activity and high Al_2O_3 and TiO_2 activities should promote the incorporation of the latter components in pyroxene. However, the high Al_2O_3 and TiO_2 contents of the Allende pyroxenes seem well beyond the bounds of equilibrium crystallization in the synthetic systems.

Recently, however, Yang (1973) synthesized an Al-Ti-rich clinopyroxene in the $CaMgSi_2O_6$-$CaTiAl_2O_6$-$CaAl_2SiO_6$ system. The pyroxene, which contained 16-20% Al_2O_3 and 8-13 percent TiO_2, has a primary field of crystallization on the liquidus surface at 1235-1245°C at 1 atm pressure. It coexists with diopside solid solution, spinel, perovskite, anorthite, and melilite at subliquidus and subsolidus temperatures. This work suggests that a distinct and heretofore unreported species of pyroxene occurs in the composition field outlined by Yang. As its natural occurrence may be represented by the Al-Ti-rich pyroxenes in Allende, a further investigation of these pyroxenes has been carried out.

Allende Al-Ti-Rich Pyroxenes

The Allende meteorite contains a variety of pyroxenes (Clarke *et al,* 1970). The matrix consists largely of iron-rich (averaging Fa_{50}) olivine with minor amounts of clinohypersthene. Many of the chondrules consist of magnesium-rich olivine and clinoenstatite. Marvin, Wood, and Dickey (1970) have recorded diopside and ferroaugite in some inclusions. However, the Al-Ti-rich pyroxenes discussed here characteristically occur in the melilite-bearing chondrules. These chondrules are remarkable for their size and unusual composition. Compared to the common olivine-rich chondrules, which normally range from 0.5-2 mm diameter, melilite chondrules have diameters up to 25 mm. They have typically igneous textures (Clarke *et al,* Fig. 33). The characteristic minerals are melilite (40-75%), pyroxene (10-35%), and spinel (10-25%); anorthite may be present, in amounts up to 15 percent, and accessory amounts of grossular, nepheline, and sodalite have been seen in some of them. Their bulk composition shows a limited range: SiO_2 25-35 percent, Al_2O_3 26-33 percent, CaO 24-33 percent, MgO 7-21 percent, TiO_2 1.0-1.5 percent. All other oxides are less than 1 percent, except FeO, which is usually in the range of 1-3 percent (some of this FeO may be derived from the iron-rich matrix, since it is difficult to prepare these chondrules completely free from matrix).

The analyses in Table 1 correspond well to the pyroxene formula. On the basis of six oxygen atoms, Ca is always very close to 1.00; Si ranges from 1.16 to 1.57, and to bring the *Z* site occupancy to 2.00, most of the Al must be in four-coordination; Ti approaches a maximum of 0.50 atoms per 6 oxygens. However, a significant feature is that the sum of the cations is less than 4 for eight of the nine analyses, and it decreases with increasing Ti; Fuchs (1971) also commented on the low sum of the cations in his analyses. However, if the analyses are recalculated on the assumption that all Ti is trivalent, the sum of cations relative to 6 oxygens is now slightly greater than 4, ranging from 4.01 to 4.08. Another indication that some of the Ti is trivalent is that in order to recalculate the analyses in terms of conventional pyroxene components, it is necessary to assume the presence of $CaTi^{3+}AlSiO_6$ as well as $CaMgSi_2O_6$, $CaAl_2SiO_6$, and $CaTi^{4+}Al_2O_6$; the percentages of $CaTi^{3+}AlSiO_6$ range from zero in analysis A to a maximum of 38 percent in analysis I. Dowty and Clark (1973) recalculated their analysis (F, Table 1) into proportions of Ti^{3+} and Ti^{4+} so that the sum of the cations was exactly 4.00; if the analysis is recalculated into pyroxene components, the result is 39 percent $CaMgSi_2O_6$, 13 percent $CaAl_2SiO_6$, 14 percent $CaTiAl_2O_6$, and 34 percent $CaTiAlSiO_6$.

Dowty and Clark adduced direct evidence for the presence of Ti^{3+} in their Allende pyroxene from its optical properties, as represented by the polarized visible-region absorption spectra. They noted the intense color and pleochroism (dark green to brownish red), which is similar to the color reported for synthetic $NaTiSi_2O_6$ pyroxene (Prewitt, Shannon, and White, 1972), for which the valence state is undoubted because of the total chemistry. Actually the color of these Allende pyroxenes in thin sections varies with the Ti content. Of the specimens in Table 1 which I have examined, A and C are colorless, E is pale green-gray and weakly pleochroic, and F and H have the color and pleochroism described by Dowty and Clark. From the optics, therefore, it appears that the ratio of Ti^{3+} to Ti^{4+} increases as the total Ti increases; Ti^{3+} is relatively insignificant in specimens with 6 percent or less TiO_2

In Figure 1 the analyses from Table 1 are plotted in terms of the pyroxene components, the two titanium-bearing components being added and considered as a unit. The limits of solubility of $CaAl_2SiO_6$ and $CaTiAl_2O_6$ in $CaMgSi_2O_6$, as established by synthetic studies at 1 atm pressure, are indicated on this diagram. The Allende pyroxenes clearly fall far outside the limit for Di_{ss}. As there is no evidence for the crystallization of Allende pyroxenes at high pressure, this factor cannot be responsible for their high Al content. Moreover, Yagi and Onuma (1967) showed that increasing pressure diminished the solubility of $CaTiAl_2O_6$ in diopside.

The data on TiO_2 and Al_2O_3 contents are plotted in Figure 2, along with a number of partial analyses of additional Allende pyroxenes, which were made in order to further explore their range of composition. These partial analyses further define the range of compositions established by the analyses in Table 1, but do not extend it. The range of compositions of the synthetic preparations of Yang (1973) is also indicated in Figure 2. It centers on the Allende pyroxene compositions, but is not as extensive.

A significant feature of the compositional field established in Figure 2 is the relatively restricted range in Al_2O_3 (16-22%), in contrast to the wide range in TiO_2 (3.9-17.7%). Another possibly significant feature is a compositional gap between 12 percent and 15 percent TiO_2. This gap corresponds to a hiatus in optical properties between the colorless or pale-green specimens with low-to-medium Ti content and the dark green pleochroic specimens with high Ti content. A search for occurrences of both varieties in a single chondrule was unsuccessful. There is also a significant difference in crystallization sequence in chondrules with these different varieties of pyroxene. In chondrules with low-to-medium-Ti pyroxene, the crystallization sequence is spinel- melilite-pyroxene; in those with the high-Ti pyroxene it is pyroxene-spinel-melilite, and the pyroxene frequently contains cores of rhönite, which is restricted to these chondrules. Whereas the low-to-medium-Ti pyroxenes were the last phase to crystallize in the chondrules containing them, the high-Ti pyroxenes were among the first phases to crystallize. Thus the high-Ti pyroxenes appear to be considerably more

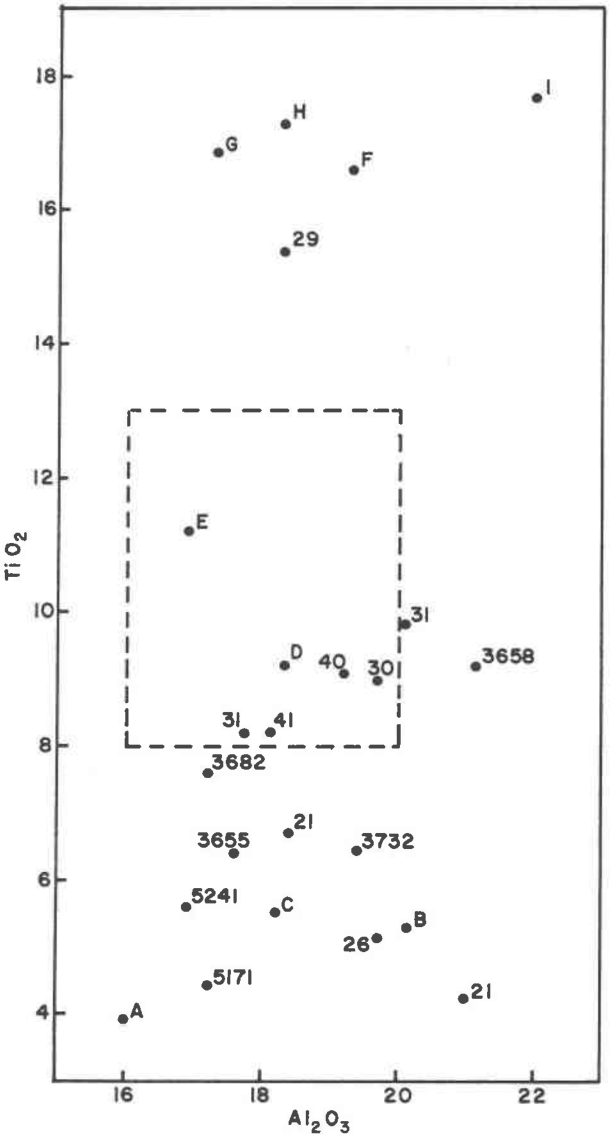

FIG. 2. Relationship between TiO_2 and Al_2O_3 weight percentages in Allende pyroxenes. Letters refer to analyses in Table 1, four-digit figures are USNM catalog numbers, two-digit figures are individual chondrules from USNM 3529. The dashed area is the composition field for the synthetic pyroxenes prepared by Yang (1973).

refractory, because of either the high Ti content or the high Ti^{3+}/Ti^{4+} ratio.

Some preliminary data have been obtained on the composition of melilite coexisting with these pyroxenes. Melilite gains in these chondrules generally show moderate compositional zoning, with Mg and Si increasing and Al decreasing from center to margin, but an approximate mean can be established. The data for all the chondrules analyzed show that the amount of the åkermanite component ($CaMgSi_2O_7$) ranges from about 20 to 70 percent and increases with decreasing Ti content of the associated pyroxene; this parallels increasing MgO in the pyroxene, as might be expected.

I believe the data presented in this paper provide sufficient evidence for the occurrence of a new species of pyroxene, defined by the synthetic studies of Yang (1973), but with a more extensive composition range. There may indeed be two new species, one with low-to-medium Ti content and the other with considerably higher Ti content, but additional evidence is necessary to establish this. [It may be significant that in Figure 1 the analyses with high Ti all plot at 50 percent ($CaTiAl_2O_6$ + $CaTiAlSiO_6$)]. The Allende pyroxenes are all essentially pure CaMgAlTiSi compounds. To what extent diadochic elements, such as Fe, may be accommodated in this phase remains to be seen. However, it is premature to propose a new name at this time, for the nomenclature of the pyroxene group is under consideration by the International Mineralogical Association.

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