A SEARCH FOR TRIVALENT TITANIUM IN APOLLO 17 PYROXENES.
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Following the discovery of substantial amounts of Ti^{3+} ions in orange soil 74220 (1), we have attempted to establish the presence of this reduced oxidation state of titanium in pyroxenes from Apollo 17 rocks 70017, 71055, and 74275. We present here evidence for trivalent titanium in these Apollo 17 pyroxenes, based on absorption spectral measurements, electron microprobe analyses of pyroxene phenocrysts, and Mossbauer spectroscopy of pyroxenes separated from crushed rock.

Microprobe analyses representative of the pyroxenes studied are summarized in table 1. There is a general trend of decreasing crystallinity, increasing titanium content, and increasing "redness" from cinnamon-brown to red in the rock sequence 70017, 71055, and 74275. The pyroxenes are subsilicic, but there is generally sufficient aluminum present to fill the tetrahedral sites. All the iron is reported in the divalent state: Mossbauer spectroscopy of the hand-picked pyroxene separates failed to detect any ferric iron, which (if present) must be below the detectibility limit of 1% Fe^{3+} in the total Fe. This eliminates the need to consider an acmite ($NaFe^{3+}Si_2O_6$) component. The Na and Mn concentrations are generally low, but there are significant amounts of Cr in the pyroxenes from all three rocks. In the crystal chemical analyses summarized in figure 1, we assume that only Al^{3+} occurs with Si in the tetrahedral sites. Chromium is thus assumed to be contained in the components $R^{2+}CrSiAlO_6$ and $NaCrSi_2O_6$, which accounts for all the sodium and eliminates consideration of an $NaTi^{3+}Si_2O_6$ component. Ti(III) and Ti(IV) are then represented by components $R^{2+}Ti^{3+}SiAlO_6$ and $R^{2+}Ti^{4+}Al_2O_6$, respectively, corresponding to the well-known ratios Ti:Al = 1:1 and 1:2, respectively (2). The microprobe data plotted in figure 1 on the basis of these assumptions and idealized components fall between these ratios, suggesting that significant amounts of titanium occur as Ti^{3+} ions in the Apollo 17 pyroxenes.

The presence of Ti^{3+} ions was confirmed by measurements of the electronic spectra in the visible region. Figure 2 shows the spectrum of an intense red pyroxene in rock 74275. The broad intense band centered around 21,000 cm^{-1} is attributed to Ti^{3+} ions, and is located on the absorption edge of an oxygen → metal (Fe^{2+}, Ti^{3+}, Ti^{4+}) charge transfer band centered in the near ultraviolet (3). The band at 21,000 cm^{-1} in lunar pyroxenes has been attributed to an $Fe^{2+} \rightarrow Ti^{4+}$ intervalence charge transfer transition (4). However, we assign it to a crystal field transition in Ti^{3+} by analogy with a similar broad spectral feature measured (4, 5) in the Ti^{3+} fassaite from the Allende meteorite. The complimentary crystal field band around 16,000 cm^{-1} arising from Ti^{3+} ions in the distorted pyroxene M1 sites (6) is obscured by the absorption edge descending into the visible region. The spectral data confirm the evidence cited earlier (7) for traces of Ti^{3+} ions in certain Apollo 11 and Apollo 15 pyroxenes. Work in progress is aimed at establishing Fe^{2+}/Ti^{3+} ratios and assigning, unambiguously, assignments of electronic transitions from high pressure absorption spectroscopy of the lunar minerals (8).

References

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Table 1. REPRESENTATIVE ANALYSES FOR APOLLO 17 PYROXENES

	SiO_2	Al_2O_3	FeO	MgO	CaO	Na_2O	TiO_2	MnO	Cr_2O_3	TOTAL
70017										
(1)	48.43	4.17	8.55	15.54	18.45	0.16	3.07	0.14	0.97	99.48
(2)	48.05	4.47	8.66	15.15	19.03	0.06	3.41	0.97	0.00	99.82
(3)	48.20	4.33	8.46	15.38	18.43	0.17	3.27	0.22	1.13	99.59
(4)	49.00	4.19	8.79	15.39	17.95	0.00	2.99	0.17	1.11	99.58
Av.12	48.66	3.96	9.20	15.29	17.97	0.10	3.03	0.25	0.79	99.25
71055										
(1)	47.39	5.14	9.49	13.62	18.66	0.14	3.89	0.20	0.91	99.43
(2)	47.78	5.17	9.42	13.82	18.62	0.11	4.00	0.13	1.02	100.06
(3)	51.32	2.16	10.65	16.36	16.25	0.07	2.27	0.20	0.65	99.93
(4)	46.14	5.64	8.91	14.29	18.72	0.06	4.92	0.23	0.98	99.89
Av.18	47.97	4.53	9.42	14.81	18.00	0.08	3.65	0.20	0.87	99.53
74275										
(1)	45.81	5.89	9.11	11.99	20.52	0.20	5.38	0.24	0.78	99.91
(2)	45.84	7.09	10.14	12.63	19.09	0.02	4.93	0.25	0.49	100.47
(3)	44.70	7.25	10.20	12.14	19.30	0.14	5.29	0.20	0.80	100.02
(4)	45.31	7.09	10.35	12.16	19.03	0.06	5.43	0.21	0.83	100.48
Av.11	45.01	6.73	9.89	12.23	19.49	0.12	5.39	0.20	0.78	99.84

Ti^{3+} in Apollo 17 Pyroxenes

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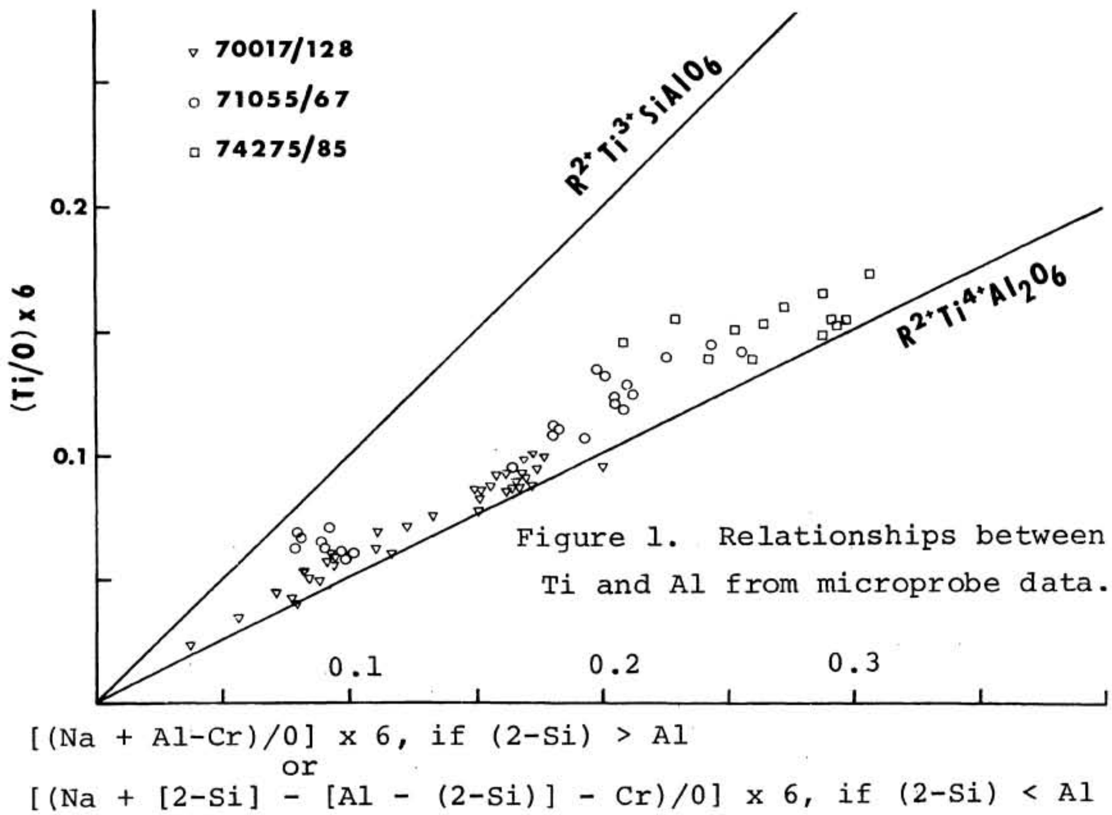

Figure 1. Relationships between Ti and Al from microprobe data.

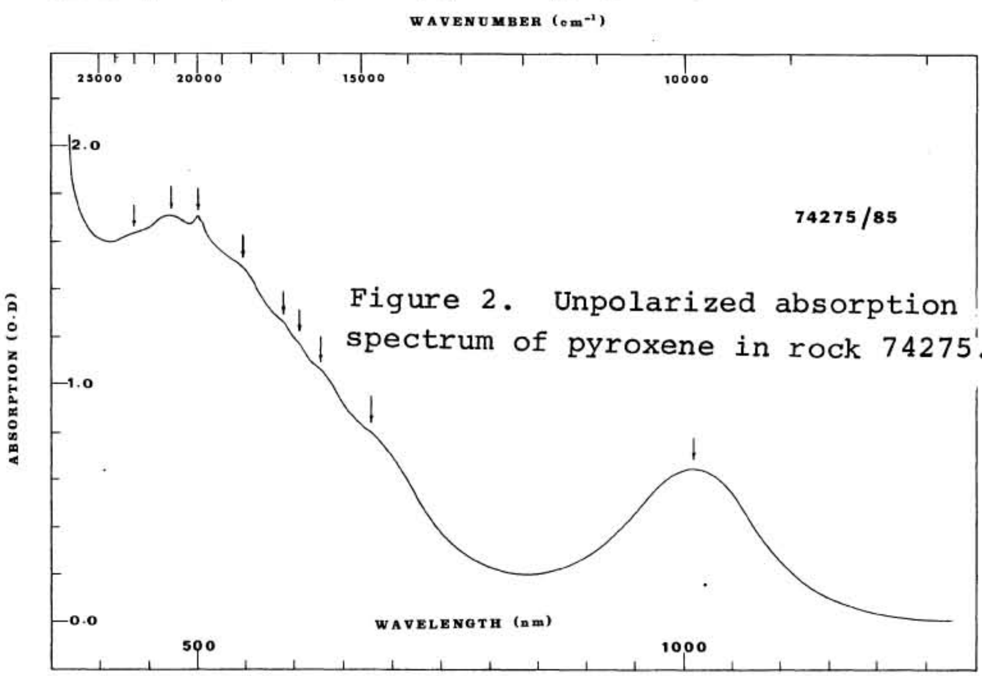

Figure 2. Unpolarized absorption spectrum of pyroxene in rock 74275.