

## PYROXENES FROM LUNAR HIGH-TI MARE BASALTS: OXYGEN ANALYSIS BY ELECTRON MICROPROBE AND ESTIMATES OF $Ti^{3+}/Ti^{4+}$

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**Introduction.** Analysis of oxygen on the electron microprobe has been seldom done in the past. The measurement of oxygen (and other light elements) has its share of unique problems, such as weak signal due to the low fluorescence yield of low atomic numbers and the high absorption of their x-rays, along with other problems that have led to the usual condition in mineral analysis of calculating oxygen from the stoichiometry of the mineral analyzed. However, with the advent of synthetic multi-layer analyzing crystals with large d-spacing and improved matrix correction methods, the direct measurement of oxygen can yield additional information. For example, by measuring O on hydrous minerals and glasses, close estimates of  $H_2O$  can be reached. In anhydrous minerals, in which one or more constituents have variable oxidation states, the valence states may be determined by calculation from the oxygen analysis. Here we attempt to measure oxygen in pyroxene from Apollo 17 high-Ti mare basalt 74275. This is a quickly-cooled basalt with  $TiO_2 \approx 13$  wt% and  $TiO_2$  in pyroxene  $>6.0$  wt% [1]. Our goal in this study is to estimate  $Ti^{3+}/Ti^{4+}$ .

**Methods.** Oxygen was measured by x-ray wavelength dispersion (WD) on the electron microprobe using a synthetic Si-W crystal (LDE1 from Ovonic) with a 2d spacing of 60.08 Å. Analyses were compared at two accelerating voltages: once at 10 kV in order to reduce the absorption correction for oxygen (which results in a low overvoltage for Fe  $K_{\alpha}$ ) and again at 15 kV, which increases the absorption correction for O  $K_{\alpha}$  but provides adequate overvoltage for Fe  $K_{\alpha}$  x-rays. A beam current of 50 nA was used in both cases. Matrix corrections used a  $\phi\rho z$  correction program [2]. Natural minerals, in which oxygen was analyzed by fast neutron activation analysis (FNAA) by McGuire et al. [3], were used as oxygen standards. Other minerals were used as standards for the remaining elements. Because carbon is a strong absorber of O  $K_{\alpha}$  x-rays, a minimum thickness of carbon coat is applied to the sample, about 100-150 Å, and care is taken to apply the same thickness to the standard.

**Results.** In order to test the oxygen analyses, mineral standards with known oxygen values were first measured. In measuring light elements, including oxygen, peak shape and spectral position are effected by local bonding conditions, such that one compound may have a different peak shape than another; this is a chemical effect [4]. If the standard is not identical in chemistry to the sample, this peak shape alteration needs to be taken into account. The use of integrated peak areas will account for these chemical effects [4]. However most automated microprobe WD spectrometers will measure peak height only. An area peak factor (APF) can be used to relate the peak height to the peak area for a given spectrometer under specific analytical conditions [5]. For the analysis of the various standard minerals, the APFs were calculated for each mineral, relative to a corundum standard. The k-ratios were multiplied by these factors in order to correct for any peak shape changes between the mineral sample and the corundum standard. Five standards are compared in Table 1. The first three are from the suite of standards in which oxygen was measured by FNAA [3]. The actinolite and tremolite are University of New Mexico standards in which O was calculated from the stoichiometry. The measured oxygen values for all five standards have a relative error of  $<3\%$ . For the standards with measured oxygen, the error is around 1%. The analysis of oxygen at 15 kV compared very favorably with those at 10 kV, despite the fact that the O absorption correction is less at 10 kV. Similar observations have been made by Armstrong [6].

A total of 26 high-Ti augites were analyzed on two sections from the mare basalt sample. Enstatite was used as an oxygen standard, with an APF correction (1.008) to account for the difference between the enstatite standard and the augite sample material. The results are presented in Table 2. The charge balance was calculated for Ti in both the +4 and +3 oxidation states. By balancing the two states to equal the negative charge of the measured oxygen, one can calculate the ratio of  $Ti^{3+}/Ti^{4+}$ . However, simple observation of the results of Table 2 indicates that the Ti

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must be in the +4 state in order to balance the negative charge. There is still a slight charge deficit, which is within the limit of error on the oxygen analysis, assuming even a 1% error. Therefore one must conclude that very little of the Ti is in the +3 state, or the deficit would increase. As a check, two other calculations were made: the difference between the measured O and the calculated O for both  $Ti^{4+}$  and  $Ti^{3+}$ , and the cation totals for both assumptions. Again Table 2 shows that the difference in calculated vs. measured O is much worse assuming  $Ti^{3+}$ . The cation total is also too high when all  $Ti^{3+}$  is used. Thus when considering the charge balance equation for pyroxene "others" components in lunar mare pyroxenes, it is perhaps safe to assume the substitutional couple  $VI Ti^{4+} \rightarrow 2IV Al^{3+} \gg VI Ti^{3+} \rightarrow IV Al^{3+}$ .

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**References:** [1] F.N. Hodges and I. Kushiro (1974) *Proc. 5th Lunar Sci. Conf.*, 505; [2] J.T. Armstrong, *Microbeam Analysis—1981*; [3] A.V. McGuire et al. (1992) *Am. Min.*, **77**, 1087; [4] G.F. Bastin & H.J.M. Heijligers (1990) *Scanning*, **12**, 225; [5] G.F. Bastin & H.J.M. Heijligers (1986) *J Micro Spectrosc Electron*, **11**, 215; [6] J.T. Armstrong, *Microbeam Analysis—1988*, 301.

Table 1. Analysis of standard minerals (Ave. 5 analyses each).

	Element Wt%											Total	Publ. O	Diff. O%
	Si	Al	Ti	Mg	Fe	Mn	Ca	Na	K	Meas. O	H			
Musc.	20.50	18.85	0.09	0.24	1.40	0.04	0.00	0.39	8.85	49.75	0.43	100.49	50.15	-0.80
Bio.	16.09	7.60	1.72	3.65	19.78	0.90	0.00	0.04	7.87	42.87	0.31	100.83	42.37	1.18
Kaers.	18.61	7.42	3.11	7.41	8.72	0.12	7.33	2.17	1.21	43.21	0.01	99.32	42.87	0.79
Actin.	26.19	0.86	0.00	12.38	4.66	0.20	8.61	0.48	0.00	44.82		98.21	43.60	2.82
Trem.	27.50	0.00	0.00	15.11	0.13	0.00	9.56	0.16	0.10	46.22		98.78	45.10	2.48

Minerals: muscovite, biotite, kaersutite, actinolite, and tremolite.

Table 2. Augite from lunar sample 74275 (Ave. 26 analyses).

Element Wt%											
Si	Al	Ti	Cr	Mg	Fe	Mn	Ca	Na	O	Total	
20.86	3.85	3.14	0.48	7.25	7.49	0.17	13.68	0.08	42.87	99.86	
Charge Balance			Delta O (Meas. O - Calc. O)				Cation Total (6 oxy)				
(Ti4+)	(Ti3+)	Oxy	As TiO <sub>2</sub>	As Ti <sub>2</sub> O <sub>3</sub>			w/ TiO <sub>2</sub>	w/ Ti <sub>2</sub> O <sub>3</sub>			
+5.26	+5.18	-5.30	0.90	1.42			3.981	4.031			