6

THE EFFECT OF FERRIC IRON ON THE ELECTRICAL CONDUCTIVITY OF OLIVINE

Al DUBA * and Jun ITO

Hoffman Laboratory, Harvard University, Cambridge, Massachusetts 02138, U.S.A.

John C. JAMIESON

Department of the Geophysical Sciences, University of Chicago, Chicago, Illinois 60637, U.S.A.

Wet chemistry and Mössbauer techniques indicate that the major chemical difference between olivines whose electrical conductivities differ by several orders of magnitude is the oxidation state of iron in the olivine. Below 1100°C, activation energies less than 1 eV are associated with the presence of Fe^{3+}, while energies greater than 1 eV occur for olivines with no detectable Fe^{3+}.

1. Introduction

The electrical conductivity σ of olivine is an important parameter to consider in the estimation of the temperature of planetary interiors based on σ profiles inferred from extraterrestrial magnetometer surveys [1] and on the more traditional σ profiles of the earth as determined by geomagnetic and magneto-telluric methods [2, 3]. The most prominent feature of the electrical conductivity of olivine is its strong temperature dependence.

If log σ of olivine is plotted against reciprocal temperature, the resulting graph is composed of one or more straight lines [4]. Thus the σ of olivine, an excellent insulator at room temperature, may be expressed as

$$\sigma = \sum_x \sigma_x \exp(-A_x/kT) \tag{1}$$

where σ_x is a pre-exponential constant, A_x is an activation energy, k is the Boltzman constant, T is the temperature in degrees Kelvin, and the summation with respect to the subscript x indicates that several mechanisms of σ may be present in olivine, including intrinsic and extrinsic semi-conduction, and intrinsic and extrinsic ionic conduction.

* Now at University of California, Lawrence Livermore Laboratory, California.

Wet chemical analysis [5] has indicated that the only significant chemical difference between olivines whose conductivities may differ by 2 or more orders of magnitude at any temperature was in the Fe^{3+} content. Since oxidation state determination by wet chemistry is subject to large uncertainties for small degrees of oxidation, a Mössbauer determination of the Fe^{3+} concentration was made. The Mössbauer results are presented below. Based on these results, literature data on electrical conductivity fall into 2 groups. Activation energy below 1 eV is associated with the presence of Fe^{3+} in the olivine spectra, activation energy above 1 eV is associated with no Fe^{3+} present.

2. Experimental

A detailed description of the method used for measuring σ has been published elsewhere [5, 6]. Table 1 includes the results of spectrographic, wet chemical, electron microprobe, and Mössbauer analyses of the single crystals used in that study. The microprobe was used only when there was insufficient quantity of sample for chemical analysis.

Because of the large amount of time involved, Mössbauer spectra were collected for only three olivines: the Red Sea and San Carlos olivines to check the Fe^{3+} contents implied by the wet chemical

A. Duba et al., Effect of ferric iron

Table 1
Results of Spectrographic, Electron-Microprobe, Mössbauer, and Wet Chemical Analyses of Olivine Samples. (Mössbauer results for Fe_2O_3 are given in brackets beside wet chemistry determination.)

Wet chemical analyses, wt %

Oxide	San Carlos [1]	Red Sea [2]	Mt. Leura [3]	Crater Elegante [4] microprobe analysis, wt %
SiO_2	40.7	40.5	41.0	37.8
Al_2O_3	0.2	0.3	0.1	<0.2
Cr_2O_3	0.05	0.00_x	0.02	
Fe_2O_3	0.41 (0.16) [5]	(<0.3)	0.34	(0.49)
FeO	7.94	9.16	7.5	24.2 [6]
MnO	0.12	0.14	0.11	<0.2
MgO	50.1	49.3	50.7	37.7
CoO	0.02	0.01	0.01	
NiO	0.38	0.38	0.34	<0.2
CuO	0.02	0.00_x	0.01	
CaO	0.07	0.01	0.04	<0.1
ZnO	0.01	0.005	0.01	
Na_2O	0.01	0.02	0.01	
K_2O	0.00	0.01	0.00	
Total	100.03	99.83	100.19	

[1] 8.2 mole % fayalite; spectrographic trace elements Ti, Ba, Be, Sc.
[2] 9.4 mole % fayalite; spectrographic trace elements Ti, Ba, Ag, Sc.
[3] 7.7 mole % fayalite; spectrographic trace elements Ti, Ba, Ag, Sc.
[4] 26.4 mole % fayalite; spectrographic trace elements Ti, Ba, Ag, Sc.
[5] Present but small (≤ 0.2).
[6] Total iron determined as FeO.

analyses and the Crater Elegante olivine since its Fe^{3+} content was unknown. The Mössbauer spectra indicated that the San Carlos and Crater Elegante olivines had F.R. = $Fe^{3+}/(Fe^{2+} + Fe^{3+}$ = 0.010 ± 0.002, but the Red Sea olivine had F.R. $\leq$ 0.003, the detectable limit of the experimental method. The Mössbauer technique indicates that the samples have slightly less Fe^{3+} than determined by wet chemistry. Both the Mössbauer and wet chemistry indicate no Fe^{3+} present in the Red Sea peridot, the Mössbauer technique has just pushed the detectable limit one order of magnitude lower.

Fig. 1 is the Mössbauer spectrum for the Crater Elegante olivine. The two prominent peaks are the doublet due to Fe^{2+} at the M1 and M2 sites in the olivine structure. The small peak is the result of Fe^{3+}, the other member of the Fe^{3+} doublet is coincident with the prominent Fe^{2+} peak centered at −0.5 mm/sec.

The electrical conductivity data for the oliviness of table 1 are plotted as a function of temperature and pressure elsewhere [5, 6]. Fig. 2 includes these data in a slightly different format. The logarithm of pre-exponential σ_x of eq. (1) is plotted against fayalite content. Data points are coded as to activation energies greater or less than 1.0 eV. For the samples studied by Duba [5, 6] activation energies less than 0.9 eV are associated with the olivines having Fe^{3+}