

## THE EFFECT OF FERRIC IRON ON THE ELECTRICAL CONDUCTIVITY OF OLIVINE

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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<sup>3+</sup>, while energies greater than 1 eV occur for olivines with no detectable Fe<sup>3+</sup>.

## 1. Introduction

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

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

$$\sigma = \sum_x \sigma_x \exp(-A_x/kT) \quad (1)$$

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

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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<sup>3+</sup> content. Since oxidation state determination by wet chemistry is subject to large uncertainties for small degrees of oxidation, a Mössbauer determination of the Fe<sup>3+</sup> 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<sup>3+</sup> in the olivine spectra, activation energy above 1 eV is associated with no Fe<sup>3+</sup> present.

## 2. Experimental

A detailed description of the method used for measuring  $\sigma$  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<sup>3+</sup> contents implied by the wet chemical

Table 1  
Results of Spectrographic, Electron-Microprobe, Mössbauer, and Wet Chemical Analyses of Olivine Samples. (Mössbauer results for Fe<sub>2</sub>O<sub>3</sub> are given in brackets beside wet chemistry determination.)

Wet chemical analyses, wt %				
Oxide	San Carlos <sup>1</sup>	Red Sea <sup>2</sup>	Mt. Leura <sup>3</sup>	Crater Elegante <sup>4</sup> microprobe analysis, wt %
SiO <sub>2</sub>	40.7	40.5	41.0	37.8
Al <sub>2</sub> O <sub>3</sub>	0.2	0.3	0.1	<0.2
Cr <sub>2</sub> O <sub>3</sub>	0.05	0.00 <sub>x</sub>	0.02	
Fe <sub>2</sub> O <sub>3</sub>	0.41 (0.16) <sup>-5</sup>	(<0.3)	0.34	(0.49)
FeO	7.94	9.16	7.5	24.2 <sup>6</sup>
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 <sub>x</sub>	0.01	
CaO	0.07	0.01	0.04	<0.1
ZnO	0.01	0.005	0.01	
Na <sub>2</sub> O	0.01	0.02	0.01	
K <sub>2</sub> O	0.00	0.01	0.00	
Total	100.03	99.83	100.19	

<sup>1</sup> 8.2 mole % fayalite; spectrographic trace elements Ti, Ba, Be, Sc.

<sup>2</sup> 9.4 mole % fayalite; spectrographic trace elements Ti, Ba, Ag, Sc.

<sup>3</sup> 7.7 mole % fayalite; spectrographic trace elements Ti, Ba, Ag, Sc.

<sup>4</sup> 26.4 mole % fayalite; spectrographic trace elements Ti, Ba, Ag, Sc.

<sup>5</sup> Present but small ( $\leq 0.2$ ).

<sup>6</sup> Total iron determined as FeO.

analyses and the Crater Elegante olivine since its Fe<sup>3+</sup> content was unknown. The Mössbauer spectra indicated that the San Carlos and Crater Elegante olivines had F.R. = Fe<sup>3+</sup>/(Fe<sup>2+</sup> + Fe<sup>3+</sup>) = 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<sup>3+</sup> than determined by wet chemistry. Both the Mössbauer and wet chemistry indicate no Fe<sup>3+</sup> 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<sup>2+</sup> at the M1 and M2 sites in the olivine structure. The small peak is the result of Fe<sup>3+</sup>, the other member of the Fe<sup>3+</sup> doublet is coincident with the prominent Fe<sup>2+</sup> peak centered at -0.5 mm/sec.

The electrical conductivity data for the olivines 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  $\sigma_x$  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<sup>3+</sup>

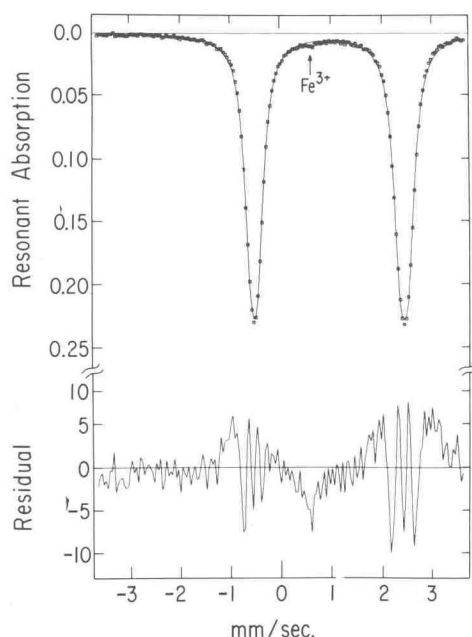


Fig. 1.  $^{57}\text{Fe}$  Mössbauer spectrum of Crater Elegante olivine at 295°K. The doublet results from  $\text{Fe}^{2+}$  at the M1 and M2 sites. The small peak at 0.7 mm/sec is assigned to the high velocity peak of a weak  $\text{Fe}^{3+}$  doublet. The low velocity peak of  $\text{Fe}^{3+}$  coincides with the low velocity peak of  $\text{Fe}^{2+}$ .

present while the olivine with no detectable  $\text{Fe}^{3+}$  has an activation energy of 1.2 eV.

### 3. Discussion

Fig. 2 is a plot of  $\log \sigma_x$  vs mole % fayalite for all available  $\sigma$  data on olivine with activation energies  $A_x$  between 0.5 and 2.0 eV. Lower  $A_x$  are restricted to temperatures less than 500°C and seem to be related to an extrinsic semiconduction. Higher  $A_x$  are reported for temperatures greater than 1100°C and are variously described as due to ionic conduction or intrinsic semiconduction [6].

Using selected literature data and data they collected for olivines with 7.4, 8.4 and 12.6 mole% fayalite (Fa 7.4, etc.) Kobayashi and Maruyama [7] propose a relationship between  $\log \sigma_x$  and mole % fayalite in olivine single crystals (line III in fig. 2) that implies an extremely high value of  $\log \sigma_x$  for fayalite ( $\log \sigma_x \cong 12$ ). If, on the other hand, all avail-

able literature data are plotted as in fig. 2, two interesting features appear:

- 1) The activation energies of all single crystal data below the line marked I are 1.0 eV or less, while above that line the activation energies are all greater than 1.0 eV.
- 2) The activation energies for all olivine powders below the line marked II are less than 1.0 eV and those above the line are greater than 1.0 eV.

For the olivines represented in fig. 2, numbers 3, 23, and 25b, c and e have  $\text{Fe}_2\text{O}_3 > 0.05$  wt%; numbers 6, 7, 21, 25d and 27 have  $\text{Fe}_2\text{O}_3 \leq 0.05$  wt%, and the  $\text{Fe}_2\text{O}_3$  concentration of the others is not reported. Single crystal data in this group plot above line I for  $\text{Fe}_2\text{O}_3 < 0.05$  wt% and below line I for  $\text{Fe}_2\text{O}_3 > 0.05$  wt%. The powders behave similarly with respect to line II with the exception of number 7 (0.04 wt%  $\text{Fe}_2\text{O}_3$ ); however, number 6 from this locality does plot above line 2. Perhaps experimental difficulties can account for this discrepancy.

The apparent "saturation" effect in  $\log \sigma_x$  as a function of fayalite content along curve II for powders may be fortuitous as point 3 provides only a lower bound at 100% fayalite. Another possibility is that most of the experiments have been performed on olivines which have been oxidized in comparable fashion in the laboratory during synthesis [3, 4]. Because of the poor statistics and experimental uncertainties, no strong argument can be made for the locus of curves I and II. However, the grouping of the data indicated by these two lines is sufficient to imply that some property other than fayalite content has a controlling influence on conductivity in olivine in the temperature range from 500 to 1100°C.

Oxidation of the San Carlos olivine [6] during  $\sigma$  measurements resulted in an increased  $\sigma_x$  with no change in  $A_x$  [5, 6]. From this information alone, one could postulate that the  $A_x$  for electronic semiconduction in this temperature range, proposed by Bradley et al. [9] and supported by Hall effect measurements [10], is 0.7 eV. However, the range in  $A_x$  for olivines below lines I and II is from 0.5 eV to 1.0 eV. This large variation in activation energy may be related to  $\text{Fe}^{3+}$  concentration, other impurities, or even dislocation density variations among olivines [11].

From the relationships observed in fig. 2, it is proposed that the conductivity of olivine below

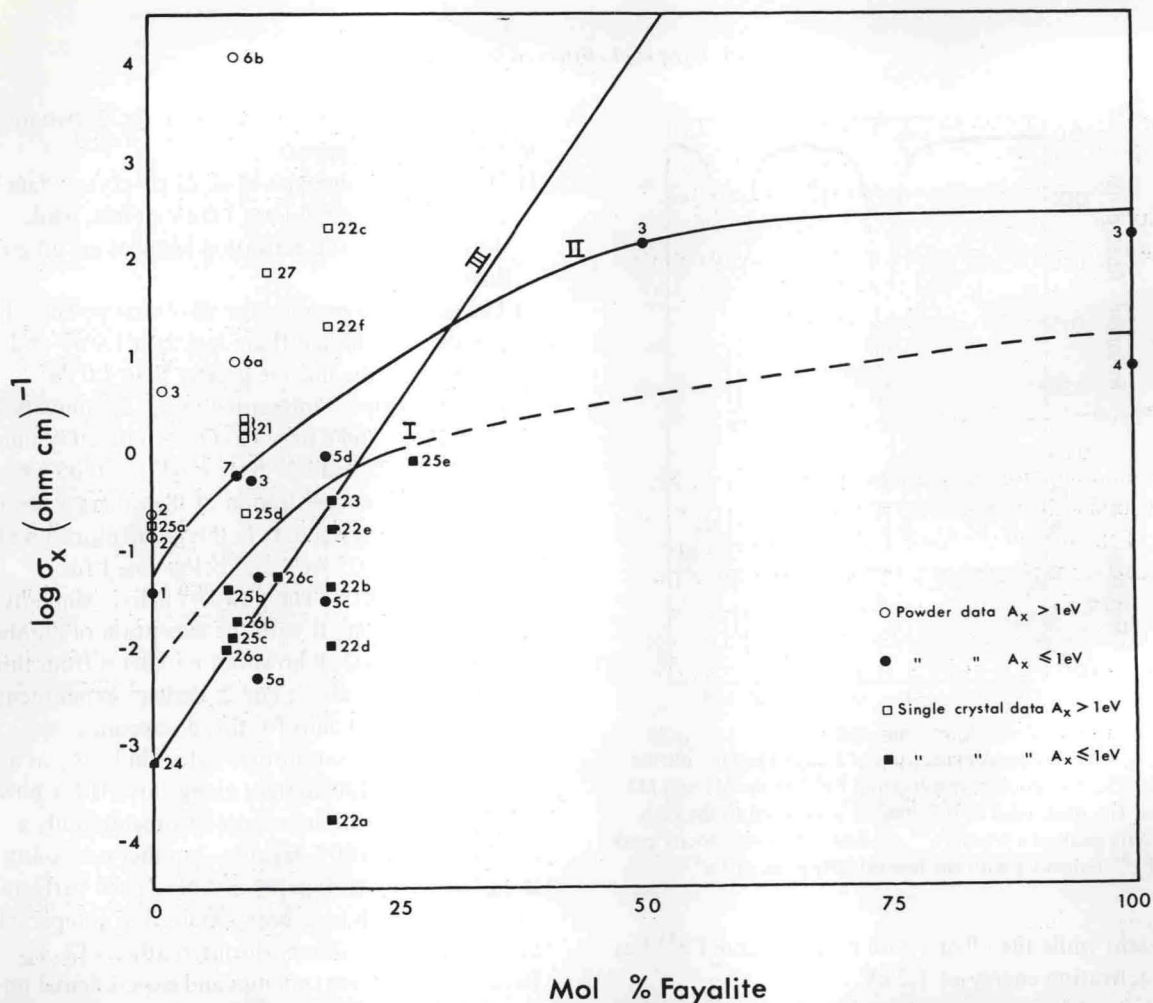


Fig. 2.  $\log \sigma_x$  vs mol % fayalite for olivine powders and single crystals. Numbers beside the data points refer to studies indicated below:

*Powders*

1. Jander and Stamm [12]. Synthetic forsterite powder, 850–1200°C,  $A_x = 0.92$  eV. 2. Hughes [4]. 2 synthetic forsterite powders. Below 900°C  $A_x$  was 1.02 and 1.43 eV. Above 900°C  $A_x$  was 3.1 and 3.3 with  $\log \sigma_x = 7$  (not graphed). 3. Bradley et al. [9]. Synthetic olivine powders, 200–700°C,  $A_x$  ranges from 1.05 eV for 1% fayalite to 0.64 eV for 100% fayalite. 4. Akimoto and Fujisawa [13]. Synthetic fayalite, 31 kb, 150–900°C,  $A_x = 0.51$  eV. 5. Hamilton [14]. Powders prepared from natural olivines, data plotted for 11.5 kb.

a) 250–450°C, 0.75 eV; b) 450–600°C, 0.91 eV; c) 250–325°C, 0.70 eV; d) 350–550°C, 0.90 eV. 6. Schult and Schober [15]. Natural olivine powder from Dreiser Weiher, Germany, 6 kb. a) 250–600°C,  $A_x = 1.28$  eV; b) 600–950°C,  $A_x = 1.89$  eV. 7. Schober [10]. Natural olivine powder from Dreiser Weiher, Germany, 20 kb,  $A_x = 0.70$  eV.

*Single crystals*

21. Hughes [4]. St. John's Island, Red Sea, Egypt, 700–1100°C, 3 sections, perpendicular and parallel to (010),  $A_x$  from 1.56 to 1.68 eV. 22. Noritomi [7]. Compositions not reported, assumed 18% fayalite by Mizutani and Kanamori [16]. Data  $\perp$  to (001) for Bonin Island not plotted since they do not differ much from (001) data which are plotted. a) Sado, Japan, 300–450°C, 0.66 eV; b) Sado, Japan 450–600°C, 1.00 eV; c) Sado, Japan, 600–1050°C, 1.64 eV; d) Bonin Island, 300–500°C, 0.64 eV; e) Bonin Island, 500–625°C, 0.80 eV; f) Bonin Island, 625–1050°C, 1.25 eV. 23. Mizutani and Kanamori [16]. Miyake-jima olivine,  $A_x = 0.86$  eV. 24. Shankland [17]. Synthetic forsterite with 0.2 mole% fayalite,  $A_x = 1.00$  eV. 25. Duba [5]. 7.5 kb. a) Synthetic forsterite, 700–1100°C, 1.70 eV. b) Mt. Leura, Camperdown, Victoria, Australia, 250–700°C, 0.85 eV. c) San Carlos Indian Reservation, Arizona, U.S.A., 150–700°C, 0.69 eV, (001). (010) and (100) data do not differ significantly and are not plotted to avoid excessive crowding. d) St. John's Island, Red Sea, Egypt, 500–1100°C, 1.21 eV, (010). e) Crater Elegante, Sonora, Mexico, 200–700°C, 0.76 eV. 26. Kobayashi and Maruyama [7]. Data were collected for the 3 principal directions for each of the olivines below. Since  $\sigma$  differs only slightly with crystallographic orientation, only one determination for each composition is plotted. a) Buhell Park, Arizona, U.S.A., 500–950°C, 0.80 eV (100). b) Buhell Park, Arizona, U.S.A., 450–950°C, 0.79 eV (100). c) Karatsu, Japan, 500–950°C, 0.81 eV (010). 27. Schober [10]. Brazil, 20 kb, 600–1300°C,  $A_x = 1.09$  eV.

1100°C is controlled by Fe<sup>3+</sup> content. Activation energies  $\leq 1.0$  eV are associated with Fe<sub>2</sub>O<sub>3</sub> > 0.05 wt%. Most likely, the mechanism is extrinsic semi-conduction due to Fe<sup>3+</sup> doping. Oxidation and reduction of the iron in natural olivine during  $\sigma$  studies to test the validity of this hypothesis have been performed and are discussed elsewhere [19].

#### 4. Geophysical application

When calculating temperature profiles from electrical conductivity-depth distributions, the oxidation state of the iron in the olivine of the mantle has to be considered. This is not a trivial problem since the equilibrium Fe<sup>3+</sup> content of mantle olivine will be controlled by both the oxidation state of the mantle and the distribution of Fe<sup>3+</sup> among the phases in the mantle.

The results of Drickamer et al. [18] may be applicable to this problem. They have shown that Fe<sup>3+</sup>  $\rightarrow$  Fe<sup>2+</sup> with increasing pressure according to the rule

$$\frac{C_{II}}{C_{III}} = K = A (P/P_0)^B, \quad (2)$$

in which  $A$  and  $B$  are constants,  $C_{II}$  and  $C_{III}$  the fraction of sites occupied by Fe<sup>2+</sup> and Fe<sup>3+</sup> and  $P_0 = 1$  kb for the values of  $B$  quoted in ref. [18].

We have plotted the 27 values for  $A$  and  $B$  given in [18] and have discovered a linear relationship between  $\ln A$  and  $B$ :

$$A = \exp(-4B), \quad (3)$$

where  $B$  varies from  $\sim 0$  to 4 while  $A$  ranges from  $\sim 0.3$  to  $10^{-7}$ . While some of the  $A$ ,  $B$  values are for temperatures other than 295°K, omission of these points does not change eq. (3) significantly. For  $B = 0$ ,  $A = 1$  and for  $A > 1$  (i.e.  $C_{II} > C_{III}$ ),  $B$  is forced to be negative and eq. (2) predicts that pressure will cause the formation of more ferric iron rather than less. Since Drickamer et al. studied substances with  $A < 1$  the validity of eqs. (2) and (3) in the region  $A > 1$  is unproven. Hence, regardless of its attractiveness for geophysical applications in studies of the oxidation state of iron compounds at elevated pres-

ures, in the case of small amounts of ferric iron being present in a basically ferrous compound, the theory is ambivalent or inapplicable.

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