THE SOURCE OF FERROMAGNETISM IN ZIRCON[1]

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Abstract

Magnetic susceptibility and magnetization measurements on more than 100 specimens of zircon from granitic rocks show weak ferromagnetic properties. Leaching, reduction, and oxidation experiments along with magnetization studies on some of these specimens indicate that the crystal grains are coated with one or more iron oxides and/or iron oxide hydrates and that the ferromagnetism is due to either or both Fe_3O_4 and $\gamma\text{-}Fe_2O_3$. The Fe_3O_4 or $\gamma\text{-}Fe_2O_3$ are not necessarily contamination brought in from outside the zircon crystals, but are formed by oxidation of natural impurity iron exposed at the grain surface to the atmosphere. Freshly broken surfaces exposing ionic iron impurity to the zircon to the atmosphere develop magnetization as a result of oxidation.

Introduction

Matumura and Koga (1963), using electron spin resonance and magnetization measurements on a colored zircon, showed that their specimen had ferromagnetic properties. Magnetic susceptibility measurements have been made in this laboratory on more than 100 specimens of zircon from granitic rocks from various localities and, with the exception of one specimen (Strangeways, Australia), all showed ferromagnetism at room temperature, confirming the results of Matumura and Koga. As pure zirconium orthosilicate ($ZrSiO_4$) is diamagnetic (-0.39×10^{-6} emu/g),[2] one must assume that this ferromagnetism is caused by some impurity, probably iron. The nature of this impurity and its association with the host crystal were examined in this investigation.

The magnetic susceptibility measurements of the zircon specimens were made within about $\pm 1\%$, using a quartz helical spring magnetic balance described previously (Senftle *et al.*, 1958; Thorpe and Senftle, 1959; Candela and Mundy, 1961). Magnetization measurements were determined by making a susceptibility versus reciprocal magnetic field plot using fields of up to 5000 oe. For convenience, the magnetization measurements are all relative values. After correcting for the ferromagnetism, the paramagnetic component of the total susceptibility was found to range from $(-0.25 \text{ to } +6.6) \times 10^{-6}$ emu/g, but most of the specimens had susceptibilities of less than 1×10^{-6} emu/g.[3] This range in susceptibility

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[1] Publication authorized by the Director, U. S. Geological Survey.

[2] Calculated from the data reported by Angus (1932).

[3] Zircon is often separated by use of a Frantz Isodynamic Separator. In terms of the table of relative susceptibilities of minerals described by Rosenblum (1958), most of the granitic zircons reported here can be separated at currents in excess of 1.5 amp. Cyrtolites. which can be separated at a lower current, are not considered in this paper.
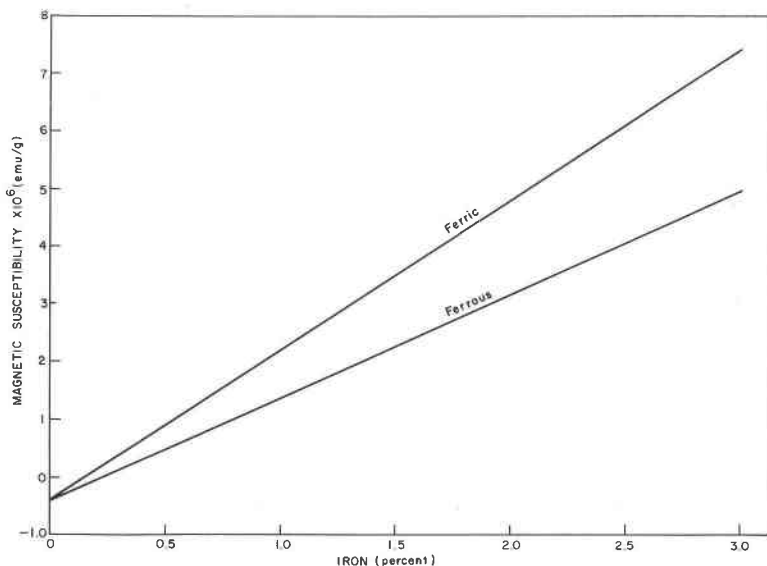
Fig. 1. Variation of the magnetic susceptibility of zircon calculated for iron in the ferrous or ferric state.

reflects the variation in the amount of paramagnetic impurity in the natural zircon.

The spectrographic analyses of granitic zircon generally show less than three per cent iron, a few hundredths per cent or less of the rare earth elements, and little or no nickel or cobalt. Undoubtedly some of the rare earths will contribute to the ferromagnetic properties, but the observed ferromagnetism is too large to be accounted for even by the most magnetic of the rare earth ions. The major part of the ferromagnetic susceptibility is therefore probably associated with iron or an iron compound present as an impurity in or on the surface. Figure 1 shows how the susceptibility of zircon would vary if the only paramagnetic impurity present were ferrous or ferric iron replacing zirconium in the zircon lattice. The range in susceptibilities is just about the same as that found experimentally for the paramagnetic component and corresponds to the amount of iron present in most zircon from granitic rocks. Although this suggests that iron may be the major paramagnetic impurity, the source of the ferromagnetism is not apparent, and the following experiments were performed to investigate the observed magnetization in more detail.

LEACHING EXPERIMENTS

Foster (1948) and Tomita (1954) have leached zircon in oxalic and hydrochloric acids, respectively, and have been able to remove the natu-
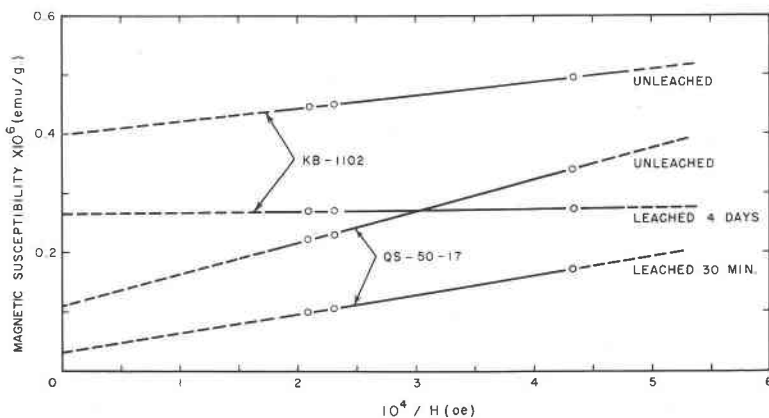
FIG. 2. Effect of leaching in warm HCl. The magnetization (slope of magnetic susceptibility vs reciprocal magnetic field plot) is reduced, and the magnetic susceptibility is lowered.

ral brown coloration. Their experiments suggest that zircon is coated with a hydrous iron oxide stain. In our experiments, the amount of stain removed was determined by magnetic measurements. The unleached specimens studied have a small magnetization ($<15 \times 10^{-4}$ emu/g), *i.e.*, they exhibit a weak ferromagnetism. After leaching in HCl, the ferromagnetism can be gradually removed, but only after several days of leaching (Fig. 2). In general, the initial leaching reduces only the paramagnetic component (intercept on the susceptibility axis), whereas prolonged leaching also reduces the magnetization or ferromagnetic component (slope of the curve) without further reducing the paramagnetic component (Table 1). The total paramagnetism is therefore in part due to a readily soluble mineral on the zircon surface and in part due to a paramagnetic constituent, probably iron, in the lattice. The data likewise indicate that the ferromagnetism is due to a difficultly soluble compound on the surface. Similar experiments with HNO_3 failed to remove either the color or the ferromagnetism. These tests suggest that the HCl leach removes first the easily soluble iron oxides such as α-Fe_2O_3, α-$Fe_2O_3 \cdot H_2O$ or γ-$Fe_2O_3 \cdot H_2O$, and second the less soluble and ferromagnetic Fe_3O_4.

TABLE 1. EFFECT OF THE LEACHING PERIOD IN HCl ON THE PARAMAGNETIC AND FERROMAGNETIC COMPONENTS OF THE MAGNETIC SUSCEPTIBILITY OF ZIRCON

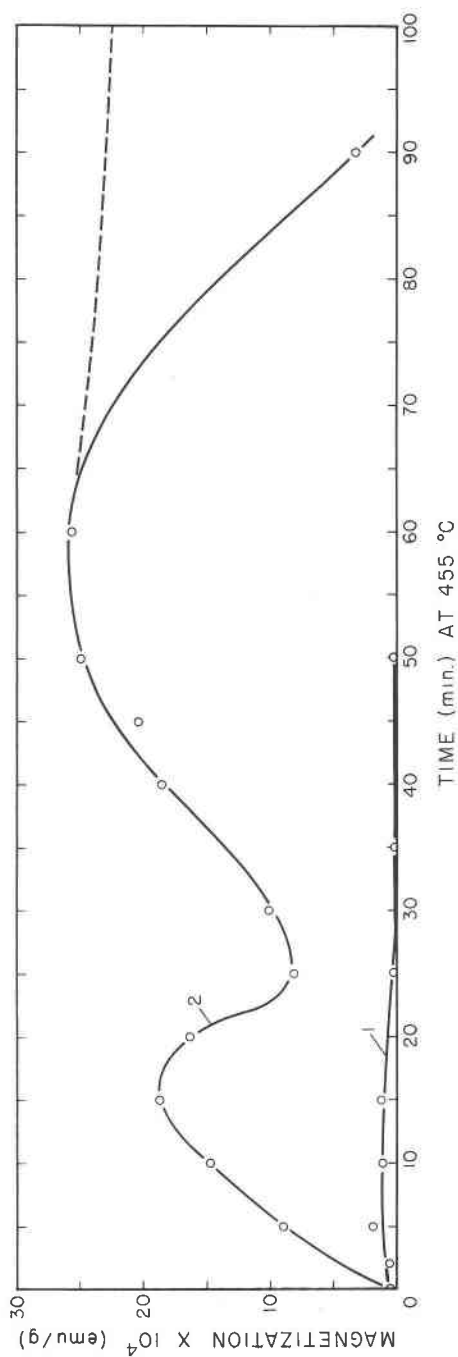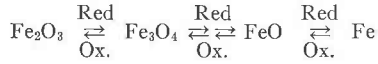|	
1. Reduction of paramagnetic component (y-axis intercept, Fig. 2)	Initial 30 min—significant Up to 4 days additional—nil
2. Reduction of ferromagnetic component (slope, Fig. 2)	Initial 30 min—nil Up to 4 days additional—significant

FIG. 3. Variation of the magnetization of a zircon (Fe<0.04%) with time of heating at 455° C. in oxygen (curve 1) and hydrogen (curve 2). Dotted line is the variation of a specimen heated 60 minutes in hydrogen followed by further heating in a vacuum.

Oxidation and Reduction at High Temperatures

The major stages in the reduction of α-Fe_2O_3 or the oxidation of iron are

$$Fe_2O_3 \underset{\text{Ox.}}{\overset{\text{Red}}{\rightleftarrows}} Fe_3O_4 \underset{\text{Ox.}}{\overset{\text{Red}}{\rightleftarrows}}\underset{\text{Ox.}}{\overset{\text{Red}}{\rightleftarrows}} FeO \underset{\text{Ox.}}{\overset{\text{Red}}{\rightleftarrows}} Fe$$

where only Fe_3O_4 and Fe show any major ferromagnetism. Reduction and oxidation of zircon followed by magnetization measurements can therefore be used to examine the nature of the oxide film on the zircon surface. When zircon is heated in oxygen at 455° C for about 50 minutes, it turns a rusty brown and undergoes slight changes in its ferromagnetic properties as shown in Fig. 3 (curve 1). The slight rise in magnetization after heating for about 10 minutes is thought to be caused by the conversion of some paramagnetic iron minerals to magnetic Fe_3O_4 or γ-Fe_2O_3, and finally to nonmagnetic α-Fe_2O_3 after prolonged heating. The small amount of ferromagnetism in hematite which is superimposed on its basic antiferromagnetism is not significant in these measurements. The rust-colored stain and the essentially nonferromagnetic properties of the specimens heated in oxygen suggested that the oxygen converted some of the impurity iron oxides to α-Fe_2O_3 which is nonferromagnetic for all practical purposes. Fainberg and Semenov (1960) also sound a similar reduction of the magnetization of limonite heated in air for prolonged periods.

When zircon specimens are heated in a reducing atmosphere at 455° C, they undergo a complex change in magnetization as shown for another specimen of the same zircon heated in hydrogen (Fig. 3, curve 2). This specimen had a very low iron content (<0.04 per cent). In specimens with higher amounts of iron, the first peak was generally higher and sharper. The general results and shape of the magnetization curve are the same for all specimens measured. Continued heating of the specimen beyond the first peak ultimately raises the magnetization, forming a second peak which is always broad. As the heating progresses beyond the first peak, the brown color of the zircon changes to black. It was observed that by heating for a period of time corresponding to that of the second peak, the sample changes from black to a gray color. A sample undergoing this amount of reduction can be almost completely bleached by leaching in strong HCl, and at the same time is accompanied by effervescence as one might expect if a metal were going into solution, with the evolution of hydrogen, or if there were occluded gas.

The only feasible explanation of these phenomena is that the heating in a reducing atmosphere (H_2) at this temperature converted the natural iron oxide and/or hydroxide coating on the zircon grains into ferromag-

netic Fe_3O_4 (first peak).[1] Continued reduction gradually converted some of the Fe_3O_4 to a nonmagnetic phase. The composition of this phase is not known. It is thought that nonmagnetic FeO is formed but, as this is metastable, it is reduced to Fe in the H_2 atmosphere. Thus, the magnetization curve shows a minimum followed by a rise due to the formation of metallic iron.

Although this is a reasonable explanation, and is in general agreement with the results of Potemkin and Grebnev (1962) who reduced bulk Fe_2O_3
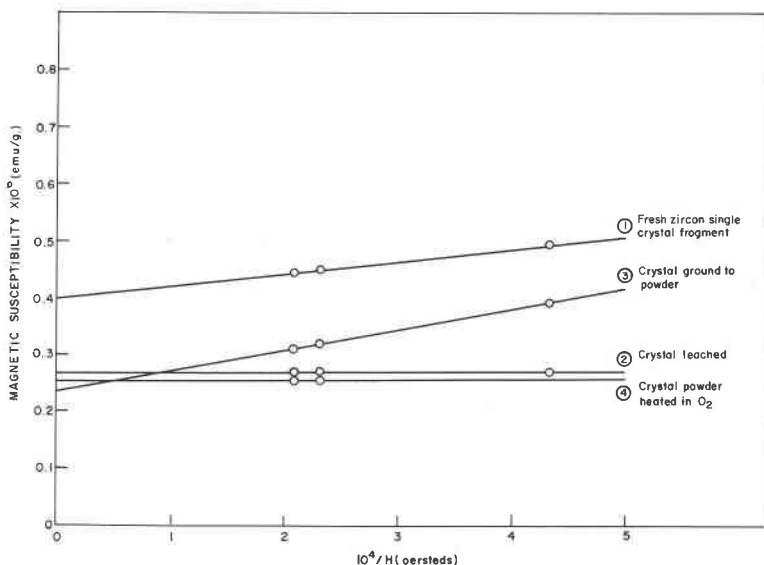

Fig. 4. Magnetic susceptibility as a function of reciprocal magnetic field for 1) a fresh zircon crystal; 2) same crystal leached in warm HCl for 4 days; 3) crystal subsequently ground to fine powder and exposed to air; and 4) crystal powder heated in O_2 at 455° C. for 30 minutes.

with C and CH_4, there is evidence that something in addition to pure metallic iron is being formed on the grain surfaces. If the second peak were due only to the formation of metallic iron, further reduction would convert more and more of the oxide to metallic iron, and the magnetization at this point (the second peak) should saturate with time of heating. Moreover, as the magnetization of Fe_3O_4 is lower than that of metallic iron, the first peak should be lower than the second peak. This is not always the case. Apparently as soon as the iron oxides are converted to metallic iron, the atomic iron starts to absorb hydrogen. It is known

[1] There is some evidence (Kojima, 1954; Aharoni et al., 1962) that the first peak is also due in part to ferromagnetic γ-Fe_2O_3.

(Smith, 1947) that hydrogen is significantly occluded by iron at elevated temperatures and that, as a result of the adsorption of hydrogen, there is a depression of the magnetic moment of the iron. This readily accounts for the low second peak and the steady decline of the magnetization observed for longer periods of heating. It also accounts for the observed effervescence when the specimen is leached in HCl. To confirm this hypothesis, a fresh sample of the same zircon used to obtain curve 2 in Fig. 3 was reduced in hydrogen until its magnetization coincided with the top of the second peak, *i.e.*, for 60 minutes at 455° C. The specimen was then further heated in steps for one hour in a vacuum rather than in hydrogen. There was no sharp drop forming a second peak, and the magnetization followed close to the dotted line in Fig. 3. Thus, it is apparent that the drop in magnetization following the second peak is due to the occlusion of hydrogen by the metallic iron, which causes a decrease in the magnetic moment.

From the general features of the oxidation-reduction curves, it is apparent that the ferromagnetic properties of zircons from granitic rocks are related to the iron compounds on the grain surfaces or along fracture surfaces and are most probably due to Fe_3O_4. The curves also show that most of the iron in the surface coating is initially in the form of α-Fe_2O_3 or one of the several paramagnetic hydrate oxide forms.

SOURCE OF THE OXIDE FILM

If the presence of an iron oxide coating on the grain or fracture surfaces of zircons from granitic rocks is a general phenomenon, as it seems to be for the zircon specimens which we have measured, it is of interest to examine the source and mechanism of the coating. Almost all zircons contain iron as an impurity. This iron could be from either or both of two sources: (1) in the original melt from which the zircon crystallized, or (2) some outside source from which, at some time after crystallization, iron migrated into the lattice. The first source seems to be the most likely, although the second cannot be ruled out. The progress of natural radiation damage (metamictization) which takes place in zircon may well enhance a diffusion process so that iron could penetrate the lattice and micro-fissures with relative ease. To clarify this question, the following experiment was performed.

An unheated single crystal of zircon was leached in strong HCl for four days until the magnetization was reduced to zero. At this point, all the Fe_2O_3 and Fe_3O_4 on the exposed surfaces will have been removed. The crystal was then carefully ground under acetone in an agate mortar to minimize the oxidation of any new iron exposed on fresh surfaces by the grinding operation. The acetone was then allowed to evaporate and the

specimen exposed to the air. Subsequent measurements showed that the magnetization was more than twice the magnetization of the single crystal before it was leached. The ionic iron impurity in zircon is paramagnetic and upon exposure to air is oxidized in whole or in part, presumably to Fe_3O_4 and γ-Fe_2O_3. To check this point the ground crystal was heated in oxygen at 455° C. for 30 minutes. The specimen was now found to have a magnetization of almost zero as would be expected if Fe_3O_4 or γ-Fe_2O_3 were oxidized to nonmagnetic α-Fe_2O_3.

The results, summarized in Fig. 4, suggest that the iron oxide coating on the exposed surfaces of zircon specimens is in part due to the surface oxidation of the original ionic iron impurity present in most zircon, but it is not clear just when the oxidation takes place. Some of the iron oxide coating may be due to migration of iron in ground water, but our experiments show that if a fresh surface containing ionic iron is formed, the iron will be oxidized by the atmospheric oxygen.

ACKNOWLEDGMENTS

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