

The diffusion of Fe^{2+} ions in spinels with relevance to the process of maghemitization

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SUMMARY. The maghemitization process, by which magnetic minerals with spinel structure become progressively oxidized but remain single phase spinels, seems to be an important feature of submarine weathering. Whether the process takes place by the minerals acquiring oxygen from the sea-water or by the sea-water leaching out iron, the controlling process is the diffusion of Fe^{2+} in the spinel structure. Magnetic studies have suggested that during maghemitization the availability for oxidation of Fe^{2+} in the tetrahedral (*A*) sites of the spinel structure is much less than that in octahedral (*B*) sites. In this study the Fe^{2+} -containing spinels FeAl_2O_4 , FeCr_2O_4 , FeGa_2O_4 , and Fe_2GeO_4 , in which Fe^{2+} is predominantly in either *A* or *B* sites were prepared, and the diffusion of Fe^{2+} was studied by (1) interdiffusion experiments with the Mg^{2+} counterparts and (2) oxidation experiments in air. Fe_2GeO_4 (Fe^{2+} in *B* sites) was found to be associated with a higher interdiffusion coefficient and lower activation energy than FeAl_2O_4 (75% Fe^{2+} in *A* sites). Oxidation/diffusion activation energies of 0.27 and 0.71 eV were assigned to Fe^{2+} in *B* and *A* sites respectively. The experiments thus provide support for the maghemitization model in which Fe^{2+} in *B* sites is preferentially oxidized.

THE titanomagnetites ($\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$, $0 < x < 1$) and their alteration products are the principal carriers of the palaeomagnetic record in the vast majority of igneous rocks and many other materials of palaeomagnetic and archaeomagnetic usefulness. One alteration process, which has attracted interest for over two decades, is low temperature oxidation maintaining the original spinel structure. The cation-deficient oxidation products are called the titanomaghemites and the oxidation process, 'maghemitization'. Interest in maghemitization has accelerated over recent years as advancing exploration technology has enabled the recovery of basalt samples from the ocean floors where conditions seem especially to promote the process. The degree

and extent of maghemitization appears generally to increase with increasing age, which corresponds to increasing distance from mid-oceanic ridges (spreading centres). Thus Ozima *et al.* (1974) on the basis of chemical and magnetic studies of sea-floor basalts from a number of locations infer an increasingly deep maghemitized layer extending to several hundred (i.e. $n \times 10^2$) metres in depth after 10^8 years of submarine weathering (represented schematically in fig. 1). It also appears that the intensity of natural remanent magnetization (NRM) of submarine basalts falls rapidly with increasing distance from a spreading centre, as shown by Irving (1970), for samples recovered from the mid-Atlantic ridge at 45°N . The NRM intensities of young submarine material is very high (up to 0.1 Gauss). The magnetic mineral would be in the form of fine, monodomain particles in such quenched basalts, and studies of the intensity of thermoremanence (TRM) acquired by monodomain synthetic titanomagnetites (Özdemir and O'Reilly, 1978) are consistent with such high intensities. The variation of intensity with age may account for some features of the pattern of geomagnetic anomalies observed over the ocean basins.

It has been suggested that the maghemitization process may contribute to the fall in intensity of the initially acquired TRM and otherwise complicate the interpretation of the NRM of rocks. The simulation of the maghemitization process has therefore been attempted in the laboratory, both to obtain data which could be used to identify naturally occurring titanomaghemites and to assess the magnetic consequences of maghemitization. Finely ground sintered polycrystalline titanomagnetite has been heated in air (e.g. Readman and O'Reilly, 1970) at temperatures up to 300°C and significant degrees of maghemitization reached in times of the order of hours. The mechanism by which maghemitization proceeds has been the subject of some discussion. During maghemitiza-

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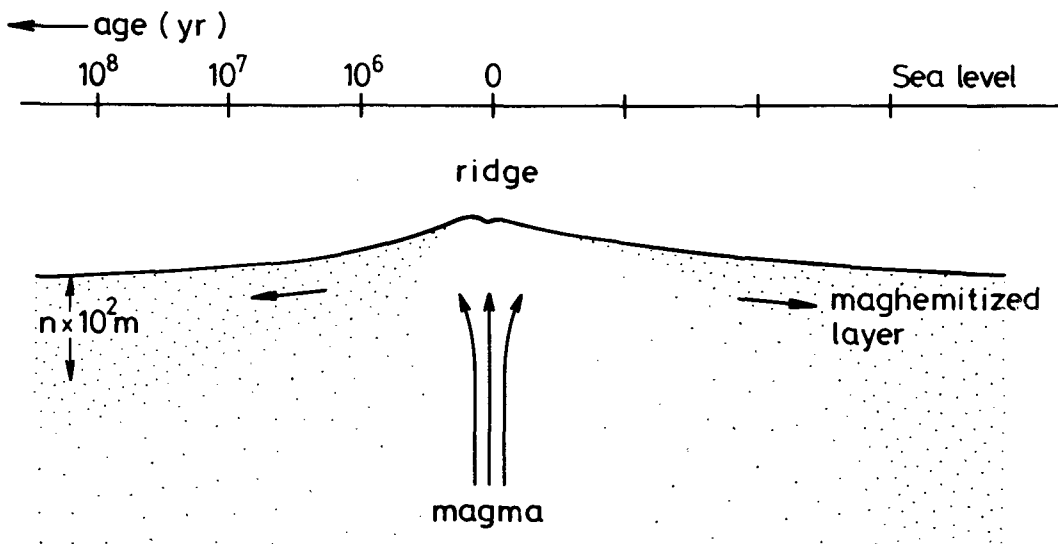


FIG. 1. Schematic picture of the evolution of the submarine crust due to weathering. The shaded region indicates the thickening with time (and distance from the spreading centre) of a maghemitized layer (see text) in which the magnetic titanomagnetite minerals become progressively more non-stoichiometric and undergo a corresponding change in magnetic properties (after Ozima *et al.*, 1974).

tion in air, oxygen atoms absorbed on the grain surface become ionized by acquiring electrons from Fe^{2+} ions diffusing through the crystal. The resulting concentration gradients thus cause the diffusion of Fe^{3+} and vacancies into the interior of the grain and the diffusion of Fe^{2+} and Ti^{4+} from the interior. The process is governed by the availability of oxygen at the surface, the energy required to release an Fe^{2+} from a lattice site, and the mobility of the diffusing ions. The availability for oxidation of Fe^{2+} located in the inequivalent sublattices of the spinel structure is not necessarily the same. It has been suggested (O'Reilly and Banerjee, 1966) that covalent bonding in tetrahedral (*A*) sites of the structure renders tetrahedrally sited Fe^{2+} less available for oxidation than Fe^{2+} ionically bound in octahedral (*B*) sites. The variation of saturation magnetization with degree of maghemitization, which is sensitive to the distribution of cations between the sublattices and which in turn reflects the mechanism of maghemitization, indicates that this may indeed be so (O'Donovan and O'Reilly, 1978).

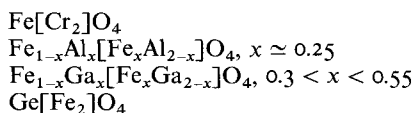
In the submarine environment, the maghemitization process may take place not by acquisition of oxygen but by the sea-water leaching out the metal ions. If it is assumed that the sea-water is saturated with oxygen and thus oxygen is not simultaneously

leached out, then, if charge balance is to be maintained within the crystal, metallic species can be removed only as atoms. Each cation must then acquire the necessary number of electrons before leaving the crystal. The only source is the extra electrons of Fe^{2+} (or any other variable valency transition-metal ion in a reduced state). Thus the removal of a Ti atom requires the oxidation of four Fe^{2+} ions to Fe^{3+} , and the removal of an Fe atom the transformation of two Fe^{2+} to Fe^{3+} . The mechanism of electron hopping between Fe ions on octahedral sites may facilitate this process in the latter case. Thus Fe would be more readily leached out than Ti and the Fe/Ti ratio would fall as the degree of maghemitization increased. At submarine temperatures, ionic diffusion rates in basalts will generally be less than in lavas in subaerial volcanic areas, and heterogeneous titanomaghemites may be commonplace with maghemitization developed to a higher degree at the grain surfaces and along cracks in the grains, as is indeed suggested by, for example, the optical micrographs of Hall and Fischer (1977). The maghemite/ilmenite intergrowths in iron ore bands in plutonic layered basic rocks (e.g. the Bushveld complex of South Africa) represent heterogeneities of a different kind (Schwellnus and Willemsse, 1943) and are discussed at some length by Basta (1953).

It is of interest to note that Basta (1953) appears to be the first to use the term 'titanomaghemite', at that time thought to be maghemite with Fe^{3+} substituted by Ti^{3+} .

The present study

The purpose of the present work is to measure the diffusion rates of ferrous iron from the two cation sites of the spinel structure. To this end, Fe^{2+} -bearing spinels were selected in which the Fe^{2+} was located principally either on one sublattice or the other. The diffusion rates were then to be studied by two methods, interdiffusion with the Mg-bearing counterpart and oxidation in air. Materials selected were chromite, hercynite, and the gallium and germanium spinels of Fe^{2+} . Denoting the occupancy of octahedral site by parentheses the cation distributions are thought to be:



These spinels and their Mg-counterparts were prepared by sintering techniques.

Sample preparation

With the exception of hercynite and the Mg-spinels, all materials were prepared from intimate stoichiometric mixtures of metallic iron, ferric oxide, and the appropriate oxide (Cr_2O_3 , Ga_2O_3 , or GeO_2), which were pressed into pellets, sealed in evacuated silica tubes, and fired following the method of Rossiter (1966). Two firings were made in each case at temperatures of 1020–1050 °C and for periods of 4 to 10 days. After the first firing the materials were reground and again pressed into pellets before the second firing. FeAl_2O_4 was synthesized by a procedure similar to that employed by Petherbridge *et al.* (1974). A mixture of Fe_2O_3 and Al_2O_3 was fired in air followed by a second firing at 1325 °C in a 1:1 mixture of $\text{CO}:\text{CO}_2$. The Mg spinels were prepared from mixtures of MgO and the appropriate oxide fired twice in air at 1050 °C.

Chemical analyses, carried out using an electron probe microanalyser (EPMA), yielded results in good agreement with the expected compositions. X-ray examination by Debye-Scherrer and Guinier de Wolff techniques confirmed that the synthesized materials were spinels, and determined unit cell edges were in good agreement with published values. None of the samples were found to be magnetic at room temperature.

Interdiffusion studies

Experimental. Diffusion couples comprised a rectangular section of the iron spinel enclosed within a pellet of its Mg counterpart. Pieces of FeAl_2O_4 and Fe_2GeO_4 were cut by diamond saw to cubes with sides approximately 2.5 mm. The faces were then ground manually on 600 grade carborundum and cleaned ultrasonically. Samples of chromite were cleaved by razor blade, whilst FeGa_2O_4 was too soft for suitable shaping. The gallium spinel, therefore, was not used for diffusion experiments. To prepare the couple FeAl_2O_4 – MgAl_2O_4 a small amount of powdered MgAl_2O_4 was placed in a 6 mm steel die and lightly compacted. A little more powder was introduced, and the FeAl_2O_4 cube was carefully located at the radial centre and pressed into the fresh powder. The remaining MgAl_2O_4 was added and a pressure of 420 kg cm^{-2} applied. This was usually sufficient to produce a pellet which remained intact after extraction, without damage to the FeAl_2O_4 . The length of the compact was approximately 8 mm. Couples of Fe_2GeO_4 – Mg_2GeO_4 and FeCr_2O_4 – MgCr_2O_4 were produced in a similar way.

Two pellets of each couple were wrapped individually in silica wool, and sealed in an evacuated silica tube. The system is approximately self-buffering with the P_{O_2} dominated by the larger quantity of Mg spinel. Diffusion runs were performed over the temperature range 800–1034 °C, for times up to 338 hours, after which the samples were cooled in the furnace. For EPMA analysis each pellet was mounted intact in Strauer's Specifix cement, and when hard, ground on 200 and 400 grade automatic laps until the centre was reached. Polishing of the discs with higher grades of carborundum and diamond paste followed. Couples of FeCr_2O_4 – MgCr_2O_4 were too soft to produce a polished surface, and the high porosity means that grain boundary diffusion is likely to dominate lattice diffusion. The interdiffusion regions were analysed, with a stepping interval dependent upon profile gradient. Two 10-second counts were recorded at each point relative to standards, and iron was measured in turn with each of the other two elements.

Although the couples are strictly ternary oxide systems, the Boltzmann–Matano method (Boltzmann, 1894; Matano, 1933) was used to calculate diffusion coefficients. This procedure is essentially a graphical method of solving the differential equation (Fick's second law) describing the interdiffusion process,

$$\frac{\delta c}{\delta t} = \frac{\delta}{\delta x} \left(\bar{D} \frac{\delta c}{\delta x} \right)$$

where c is the concentration of the diffusion element, t is time, x the (one dimensional) position coordinate, and \bar{D} , the interdiffusion coefficient, is a function of temperature T and also of c , following the relationships

$$\bar{D}(T) = D_0 \exp(-Q/kT)$$

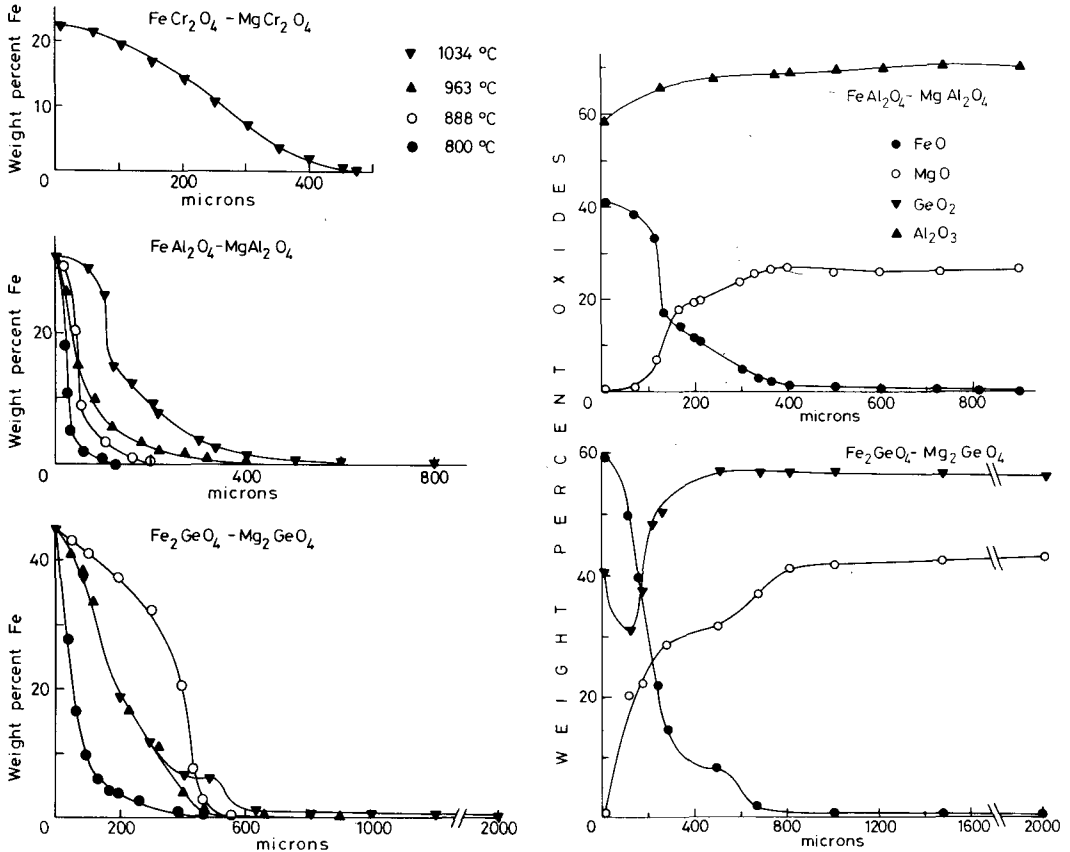
$$\bar{D}(c) = D'_0 \exp(\beta c)$$

D_0 and D'_0 are the frequency factors, Q the activation energy, and β the composition factor. $\bar{D}(c)$ at constant temperature is determined from the slopes of the interdiffusion profile (dc/dx) at each value of (c, x) and the areas ($\int_0^c x dc$) bounded by the profile and a reference plane (see, for example, Freer and Hauptman, 1978). Runs at different isotherms then provide $\bar{D}(T)$ at constant c , and

the activation energy Q may be determined. The composition-dependence of \bar{D} was examined, and activation energies were obtained for FeAl_2O_4 - MgAl_2O_4 and Fe_2GeO_4 - Mg_2GeO_4 .

Results. Typical diffusion profiles for the three systems are shown in fig. 2. Due to the poor quality of the FeCr_2O_4 - MgCr_2O_4 couple consistent analyses were only obtained at the highest temperature, 1034 °C, and, despite the higher porosity, the diffusion distance of approximately 460 μm is substantially less than that observed for the other two systems. At all temperatures diffusion of iron from Fe_2GeO_4 is further than from FeAl_2O_4 .

The complete analysis of the interdiffusion region (fig. 3) indicates the complementary nature of Fe and Mg scans. An alternative way of showing the variation across the couple is in a ternary diagram (fig. 4). It is apparent that the direct route



FIGS. 2 and 3. FIG. 2 (left). Weight per cent of iron (determined by EPMA) as a function of distance from the homogeneous iron-spinel member of three of the Fe-Mg spinel couples. The temperatures of the diffusion runs are indicated. FIG. 3 (right). Weight per cent of oxides as a function of distance from the homogeneous iron spinel member for two of the Fe-Mg spinel couples after diffusion run at 1034 °C, showing the complementary Fe and Mg profiles.

between end-members is not followed. The greatest deviation for FeO-MgO-Al₂O₃ occurs at the lowest temperature, while for FeO-MgO-GeO₂ (fig. 4) it occurs at the highest temperature. Linear diffusion paths, in general, will only be obtained when the three intrinsic diffusion coefficients are equal (Oishi, 1965). Although the systems were arranged to provide a pseudo-binary couple between FeO and MgO (one Fe²⁺ for one Mg²⁺ ion), interdiffusion between other members is possible, i.e. in FeAl₂O₄-MgAl₂O₄ there may be exchange of Fe-Al, and Mg-Al (when two Al³⁺ replace two (Fe, Mg) and a vacancy), and in Fe₂GeO₄-Mg₂GeO₄, exchange of Fe-Ge, and Mg-Ge (with two (Fe, Mg) for one Ge ion and a vacancy).

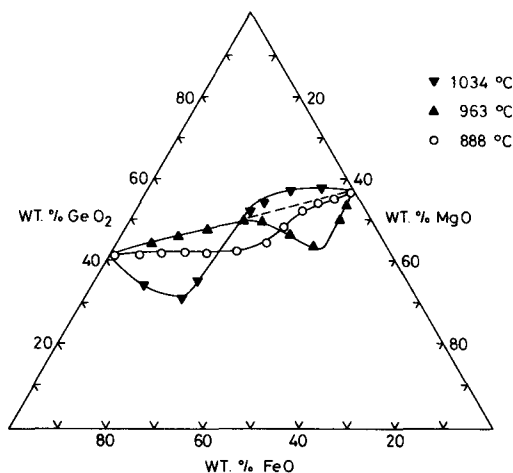


FIG. 4. Composition profiles across the Fe₂GeO₄-Mg₂GeO₄ interface after diffusion runs at the indicated temperatures, represented on an oxide ternary diagram. The direct route between end-members is not followed, the greatest deviation occurring at high temperatures.

The evaluation of interdiffusion coefficients in multicomponent diffusion is very difficult even for ternary systems described by linear differential equations (e.g. Oishi, 1965). For this reason, several authors have used the approximation of binary diffusion, and employed the Boltzmann-Matano or Wagner methods (e.g. Buening and Buseck, 1973). The spinel systems under investigation are close to constant volume and so the Boltzmann-Matano analysis was used. The composition dependence of \bar{D} is shown in fig. 5. With the exception of the run at 888 °C, Fe₂GeO₄ exhibits only a small dependence on the iron content, and the β value (change in $\ln \bar{D}$ for a complete replacement of Mg by Fe) is negative at 1034 °C.

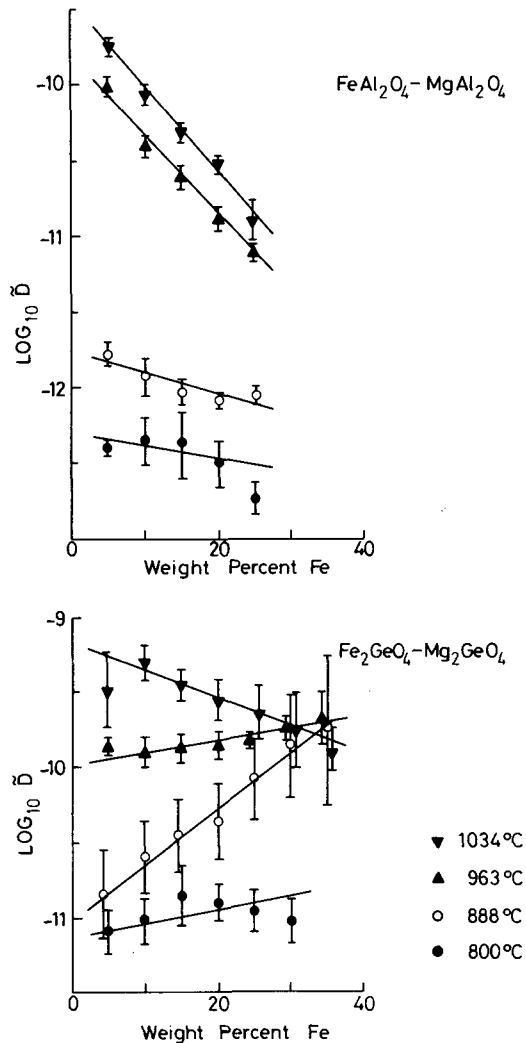


FIG. 5. The composition dependence of the interdiffusion coefficient \bar{D} , derived from the profiles of fig. 2, for Fe-Mg interdiffusion between FeAl₂O₄ and MgAl₂O₄ and between Fe₂GeO₄ and Mg₂GeO₄ at the temperature indicated.

In contrast, β for FeAl₂O₄ is negative in all cases, and increases with temperature.

The temperature-dependence of spinel interdiffusion is shown in fig. 6 and detailed in Table I. From 888 to 1034 °C the activation energy for Fe₂GeO₄-Mg₂GeO₄ decreases from 2.83 to 0.24 eV with increasing iron content. This is similar to the behaviour observed in several other oxide systems. Results for FeAl₂O₄-MgAl₂O₄ are less

consistent, but over the full temperature range Q decreases from 3.46 to 2.29 eV, which is significantly higher than for the germanium spinel at similar iron contents.

Discussion. Whilst the diffusion coefficients are sensitive to sample preparation and quality, the diffusion of iron from Fe_2GeO_4 (all iron in B site) appears to be easier than from FeAl_2O_4 (approximately 25% of iron in B site), which is possibly easier than from FeCr_2O_4 (all iron in A site). Evidence to support this proposal comes from the length of the interdiffusion profile (fig. 2) and the activation energies (Table I).

It has been assumed that the systems are approximately binary with Fe-Mg interdiffusion dominant. This assumption may now be justified. For Fe_2GeO_4 - Mg_2GeO_4 , the other possible processes are the exchange of $2(\text{Mg}, \text{Fe}^{2+})$ for Ge^{4+} . Data for the diffusion of quadrivalent cations in oxides are scarce, but two recent studies are pertinent. In titanomagnetites, $\tilde{D}(\text{Fe}^{2+}-\text{Ti}^{4+})$ is a function of P_{O_2} (Freer and Hauptman, 1978) but

from 800 to 1034 °C it appears to be significantly slower than the present $\tilde{D}(\text{Fe}-\text{Mg})$ (fig. 6). In MgO the tracer diffusion of Ge has only been measured at temperatures above 1850 °C (Harding, 1973), but the process is characterized by a high activation energy (4.0 eV) and low diffusion coefficients. Even allowing for structural and chemical differences, $\tilde{D}(\text{Mg}, \text{Fe}^{2+}-\text{Ge}^{4+})$ is likely to be several orders of magnitude slower than $\tilde{D}(\text{Fe}-\text{Mg})$ under the present experimental conditions. In the system FeAl_2O_4 - MgAl_2O_4 , exchange of Al^{3+} with Fe^{2+} and Mg is possible, but the interdiffusion of a divalent ion with a trivalent ion is likely to be very slow at these temperatures.

A complication to interpretation is the contribution of grain boundary diffusion, which will become more important with increasing porosity. A reliable test of Fe^{2+} diffusion must use couples prepared from single crystals. Unfortunately, the majority of diffusion studies on spinels in recent years have employed polycrystalline samples (see compilation of Grimes, 1972) with radioactive tracers

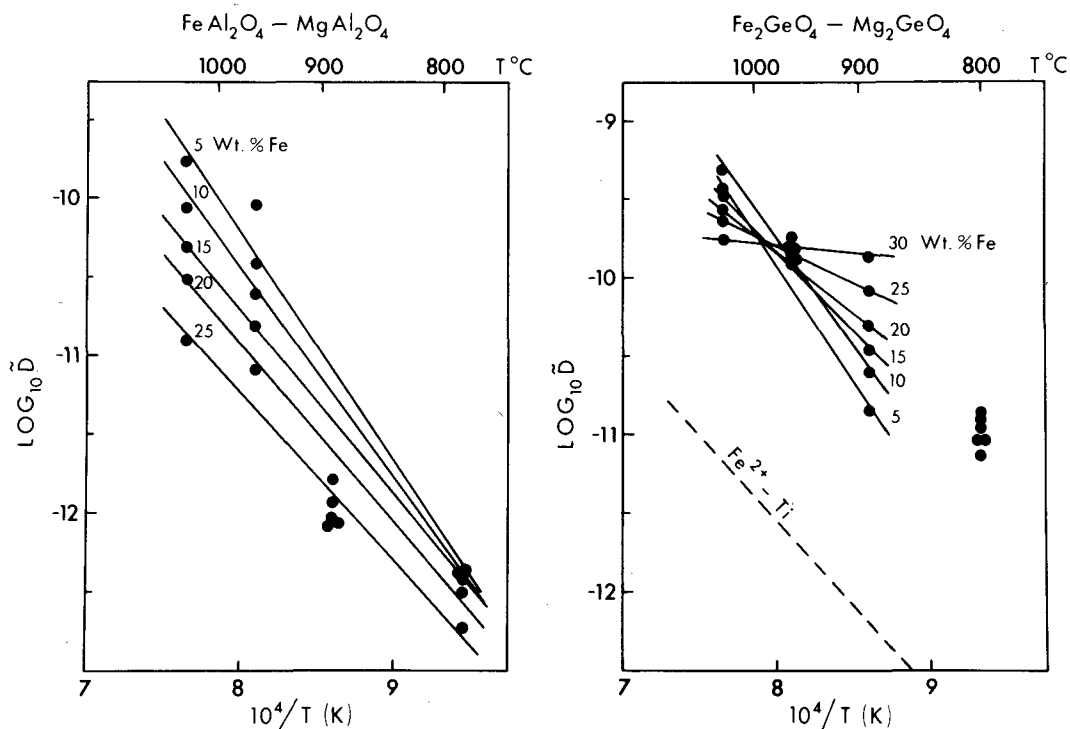


FIG. 6. The temperature dependence of the interdiffusion coefficient $\tilde{D}(\text{Fe}-\text{Mg})$ for interdiffusion between the couples at the indicated constant concentrations. Data for $\tilde{D}(\text{Fe}^{2+}-\text{Ti}^{4+})$ in the spinel structure (chain line) is based on Freer and Hauptman (1978).

TABLE I. Values of activation energies (Q) and frequency factors (D_0) for Fe-Mg interdiffusion

Wt % Fe	FeAl ₂ O ₄ -MgAl ₂ O ₄		Fe ₂ GeO ₄ -Mg ₂ GeO ₄	
	Q (eV)	D_0 (cm ² s ⁻¹)	Q (eV)	D_0 (cm ² s ⁻¹)
5	3.46 (49)	4615	2.83 (32)	33.6
10	2.97 (37)	24.6	2.68 (01)	10.6
15	2.72 (43)	1.54	2.09 (03)	4.17×10^{-2}
20	2.55 (36)	0.22	1.55 (05)	2.66×10^{-4}
25	2.29 (21)	1.09×10^{-2}	1.83 (08)	8.26×10^{-3}
30			0.24 (05)	1.55×10^{-9}

of iron thought to be in ferric or mixed valancy states.

While a spinel may be prepared containing Fe in a specific site, it is not possible to ascertain the detailed diffusion mechanism from interdiffusion experiments. Stone and Tilley (1972) analysed possible routes in spinels and noted that the most favourable path from a tetrahedral site is: tet. site—oct. hole—tet. site. If vacancies exist in the tetrahedral sub-lattice, this site should form a channel from the point of view of cation repulsion. Cations originating at octahedral sites may travel via a mixture of octahedral sites and tetrahedral holes. Ferrous iron, however, is unusual since it may be accommodated in either site, making routes harder to predict.

The purpose of this investigation was to test if interdiffusion experiments could indicate whether Fe²⁺ located respectively at *A* and *B* sites in spinels diffused at different rates. There is a strong suggestion that the *B* site iron is associated with faster diffusion and lower activation energies than *A* site iron, but the results cannot be considered as definitive. Recourse to other techniques are necessary to clarify the problem. However, in the absence of any other diffusion data, the present work may provide a useful first estimate for the three systems examined.

Oxidation studies

Introduction. A convenient technique for studying oxidation (or any reaction involving weight change) is thermogravimetric (TG) analysis performed under isothermal conditions, or with the temperature increasing at a linear rate. These are sometimes known as static and dynamic methods respectively (Blasek, 1973), or simply as isothermal and non-isothermal methods (Sestak, 1967). The present study, under dynamic conditions, examines

the behaviour of the four synthetic spinels after grinding.

Reaction kinetics. The fraction of oxidation (α) may be defined as

$$\alpha = \frac{W_t - W_0}{W_\infty - W_0}$$

where W_t is the weight of sample at time t , W_0 the weight at $t = 0$, and W_∞ the final weight. Analysis of data is usually based upon the relationship between α and time, which may be described by a general kinetic equation

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n$$

where k is the rate constant, and n the order of reaction. In turn, the temperature dependence of k is given by the Arrhenius equation.

$$k = A \exp(-Q/RT)$$

where Q is the activation energy, and R the gas constant.

Combining these equations to eliminate k , and putting $dT/dt = \gamma$ gives

$$\frac{d\alpha}{(1 - \alpha)^n} = \frac{A}{\gamma} \exp(-Q/RT)dT$$

Direct solution of this equation is not convenient, and several approximations have been proposed to evaluate Q . The main problem, however, is that n is unknown. Wilkinson (1961) described a method to estimate the order of reaction for isothermal experiments, but a suitable analogue is not available for the non-isothermal case. In one approach Freeman and Carroll (1958) provide an expression to estimate Q and n simultaneously, but the value of n is empirical, and may be meaningless. There is theoretical justification for order of reactions of 0, $\frac{1}{2}$, $\frac{2}{3}$, and 1 in solid-state kinetics (e.g. Sharp *et al.*, 1966), and these values are often substituted in the appropriate equations to test which provides the best fit. A further complication is that a single value of n will not necessarily apply to all α , and the possibility of

two processes dominating at different temperatures makes interpretation more difficult.

Reviews of a number of procedures for the analysis of reaction kinetics are provided by Sestak (1967), and Blazek (1973). The techniques may be divided into (1) differential, (2) integral, and (3) approximate methods. Two of each type are employed here. The methods of Achar *et al.* (1966) (Method I) and Dave and Chopra (1966) (Method II) lie in the first category. Coats and Redfern (1964 and 1965) (Methods III and IV) give integral methods. Finally, the methods of Fuoss *et al.* (1964) and Broido (1969) (Methods V and VI) are approximate.

Experimental. The instruments used for the thermogravimetric studies were a Stanton Mass-flow automatic Thermobalance (at the University of Newcastle), and a Stanton Redcroft Thermobalance (at the University of Strathclyde), both of which have the facility for programming a linear rate of temperature change.

Half the pellets of FeAl_2O_4 and FeCr_2O_4 were finely ground in a ball-mill under methanol for 24 hours, and dried under a lamp. Particles produced are believed to be of the order of $0.1 \mu\text{m}$ in size. Samples of FeGa_2O_4 , and the remaining hercynite and chromite were hand ground in an agate mortar and sieved to $50 \mu\text{m}$. This will be termed the coarsely ground material. TG experiments were performed with approximately 0.5 g of

spinel, at a heating rate of $1^\circ\text{C}/\text{minute}$. Three runs were made on each type of sample, and from the average results activation energies were estimated by the six methods listed above. X-ray powder photographs confirmed the existence of multiphase oxidation products in all cases.

Results. Raw data from a thermobalance run indicating the variation of weight with temperature is in the form of a smooth curve, whose gradient depends upon reaction rate. Once corrected for 'buoyancy effects', it is more instructive to plot the differential of the weight change with respect to time against temperature, the DTG curve, which for convenience is usually normalized to the starting weight. Uncertainty in the derivative is of the order $\pm 5\%$. Comparison of the curves for FeCr_2O_4 and FeAl_2O_4 (fig. 7) shows that, as expected, coarsely ground material oxidizes at a higher temperature than finely ground material. The chromite and germanium spinel, containing all iron in the tetrahedral and octahedral sites respectively, exhibit only one peak (apart from a minor one close to 300°C for the germanium spinel). The gallium spinel, with approximately half the iron in each site, has two peaks of similar size, and FeAl_2O_4 , with about 25% Fe in the octahedral site, shows a 'knee' on the low temperature side of the main peak. If it is now possible to assume that the low- and high-temperature peaks of the hercynite and gallium spinel are associated with the

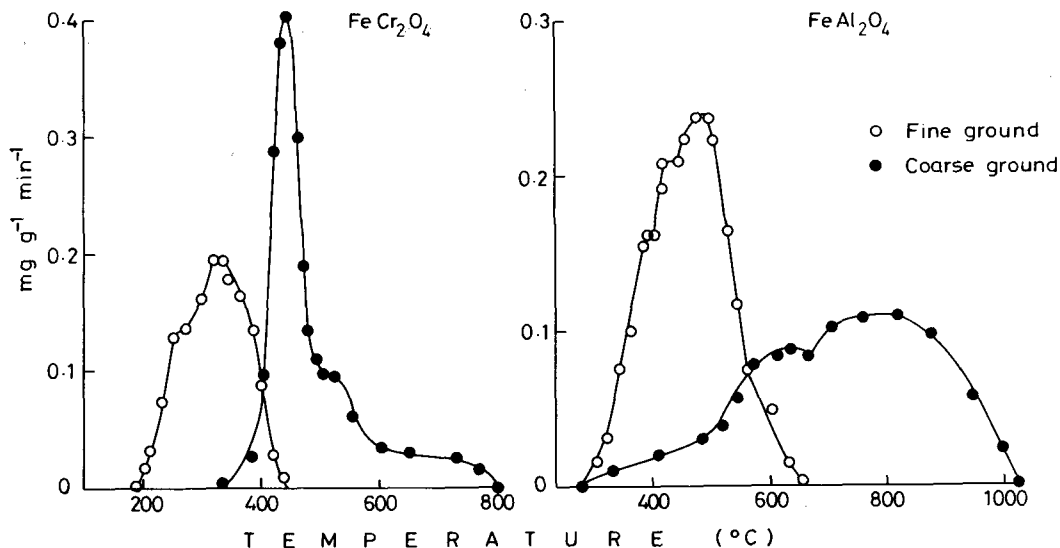


FIG. 7. Differential thermogravimetric curves for coarse ($< 50 \mu\text{m}$) and fine grained ($\sim 0.1 \mu\text{m}$) FeCr_2O_4 and FeAl_2O_4 heated in air.

TABLE II. Activation energies in eV for the oxidation of spinels during TG in air calculated by the procedures outlined in the text

Method	FeAl ₂ O ₄ (fine)		FeAl ₂ O ₄ (coarse)		FeCr ₂ O ₄		FeGa ₂ O ₄		Fe ₂ GeO ₄
	Site A	Site B	Site A	Site B	(Fine)	(Coarse)	Site A	Site B	
I ($n = \frac{1}{2}$)	0.43(08)		0.28(03)		0.38(05)	1.61(22)	0.79(02)	0.24(05)	0.38(03)
α	0.05 - 0.75		0.05 - 0.80		0.02-0.85	0.05-0.40	0.66-0.90	0.07-0.50	0.05-0.55
I ($n = \frac{2}{3}$)	0.48(07)		0.45(08)		0.42(04)	1.56(26)	0.91(02)	0.26(04)	0.44(04)
α	0.06 - 0.75		0.05 - 0.80		0.10-0.85	0.02-0.45	0.66-0.90	0.07-0.50	0.08-0.55
I ($n = 1$)	0.54(11)		0.48(80)		0.62(08)	1.13(06)		0.15(04)	0.44(04)
α	0.05 - 0.75		0.05 - 0.80		0.15-0.85	0.05-0.45		0.07-0.50	0.08-0.55
II	0.58(03)		0.47(03)		0.43(02)	2.40(07)	1.80(09)	0.47(03)	0.29(05)
III $n = \frac{1}{2}$	0.38(03)		0.31(03)		0.46(02)	2.40(07)		0.24(04)	0.28(03)
α	0.31 - 0.95		0.10 - 0.99		0.08-0.95	0.01-0.38 ^b		0.05-0.50	0.10-0.70
III $n = \frac{2}{3}$	0.45(05)		0.36(04)		0.49(02)	2.40(08)		0.26(04)	0.29(03)
α	0.31 - 0.95		0.10 - 0.99		0.08-0.99	0.01-0.40		0.05-0.50	0.10-0.70
III $n = 1$	0.60(05)		0.41(04)		0.54(02)	2.34(07)	0.50(02)	0.28(03)	0.32(03)
α	0.31 - 0.98		0.10 - 0.90		0.08-0.95	0.05-0.40	0.74-0.99	0.15-0.50	0.10-0.80
IV $\alpha < 0.3$	1.06(08)		0.48(07)		1.37(04)	2.26(16)		0.20(03)	0.14(03)
V	0.74(11)	0.33(04)	0.74(12)	0.24(04)	0.39(05)	0.60(08)	2.21(18)	0.22(02)	0.39(06) ^d
VI	0.66(04)		0.58(03)		0.68(03)	2.26(11)	0.59(08)	0.26(03)	0.41(03)
α	0.36 - 0.99		0.10 - 0.99		0.09-0.99	0.02-0.38	0.60-0.97	0.23-0.50	0.10-0.95
Average from columns above									
Site A	0.74(11) ^c		0.74(12) ^c		0.58(29)	1.89(63)	0.77(23) ^d		
Site B	0.33(04) ^c		0.24(04) ^c					0.26(08)	0.34(09)
Average ^e	0.57(20)		0.44(14)						

α Range of reaction over which Q was calculated.

(a) A small peak at 200 °C yields a Q of 0.15 eV.

(b) $Q \approx 0.25$ eV are obtained at higher α .

(c) Method V.

(d) Excluding (c).

(e) Refers to all data for FeAl₂O₄.

oxidation of iron from predominantly *B* site and *A* site respectively, then comparison may be made with the results for Fe₂GeO₄ and FeCr₂O₄, where the iron originates exclusively on one site. A compilation of the calculated activation energies is given in Table II and, as examples, plots for methods I and II are shown in fig. 8.

The general agreement between different methods is around 20%. With the exception of the results for the coarse grained FeCr₂O₄, most activation energies are in the range 0.2-1.0 eV, and some procedures are sensitive to order of reaction. Results for FeCr₂O₄ (coarse ground) and FeGa₂O₄ by method V differ appreciably from the others, but it is the only method able to separate two rates for FeAl₂O₄.

Of the integral methods, IV requires less data preparation, but as it is only appropriate for $\alpha < 0.3$ it is of limited applicability. The earlier Coats-Redfern version, III, yields results close to the

average, especially for $n = 1$, and they are not significantly different from those of method I. The variation is not systematic, but neither method was able to treat the high-temperature peak of FeGa₂O₄ for some values of n , due to curved plots.

Method II is the only one to use DTG data directly, but is probably the most inconvenient as the profiles must be integrated and differentiated. The results are, however, close to the average.

In terms of data preparation, and reliability, there is little to choose between III and I. For a rapid estimate of activation energy, V is useful, but only for relative values. Method VI is a good approximate method, and II is also recommended.

Discussion. The average activation energy for Fe₂GeO₄ of 0.34 (± 0.09) eV is substantially less than either of the values for FeCr₂O₄, and that of the coarse-ground material appears anomalously high. For a given sample, Q should be independent of particle size if the oxidation mechanism is

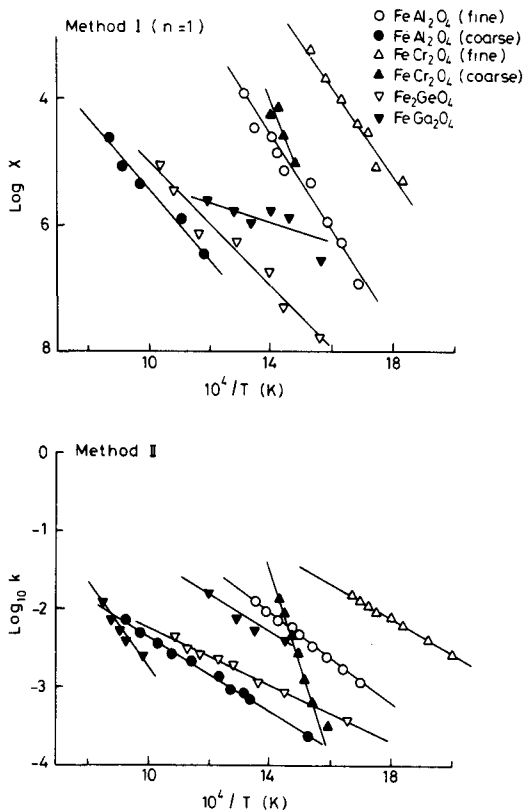


FIG. 8. Examples of the analysis of the thermogravimetric data to extract activation energies (see text).

invariant. It is possible that the fine-grained FeCr_2O_4 was strained during grinding, making oxidation easier, but conversely most of the coarse-grained FeCr_2O_4 oxidized close to 440°C , producing a sharp DTG curve (fig. 7) so the high value may be an artefact of analysis. Alternatively, the activation energies may reflect different reaction kinetics. Readman (1972) heated titanomagnetites in air and found that the oxidation products depended upon particle size: a single phase, cation-deficient spinel for the finely ground material, and multiphase oxides for the coarsely ground material. A similar behaviour was observed here for FeAl_2O_4 . The single phase cation-deficient spinels decompose at a higher temperature to a mixture of phases, with no change in bulk chemical composition (inversion). Coarsely ground material may oxidize directly to a multiphase product. In the latter case the reaction rate would be governed not only by ionic diffusion, but also by the rate of translation of phase boundaries. Different oxida-

tion mechanisms would then operate for the two grades of material.

Results for the gallium spinel indicate that an activation energy of $0.26 (\pm 0.08)$ eV is associated with the low-temperature peak, and a higher value of $0.77 (\pm 0.23)$ eV with the high-temperature peak. Although most methods of analysis were unable to resolve two processes in FeAl_2O_4 , results from V for both coarse- and fine-grained material are very close to the above values for FeGa_2O_4 , whilst the average results for the two grades of FeAl_2O_4 are $0.44 (\pm 0.14)$ eV and $0.57 (\pm 0.20)$ eV respectively. Combining activation energies which are thought to represent oxidation of octahedral site iron yields $0.29 (\pm 0.05)$ eV, and for tetrahedral site iron $0.71 (\pm 0.09)$ eV. The implication is therefore that oxidation of B site iron will be more rapid than A site iron, in agreement with the O'Reilly and Banerjee (1966) model.

The present results of approximately 0.5 eV for the oxidation of spinels containing ferrous iron are in good agreement with published data connected with the oxidation of titanomagnetites. Creer *et al.* (1970), and Petersen (1970) measured the change of magnetization with time of heating in air of basaltic rocks containing titanomagnetites, and estimated activation energies of 0.5 eV. Petersen obtained the same value from a diffusion model for the growth of lamellae. Rao and Rigaud (1975) oxidized ilmenite in the form of powder and platelets. Activation energies were 0.41 eV for the powder, in air, and 0.47 or 0.86 eV for the platelets depending upon the rate law selected. In contrast Readman and O'Reilly (1970) deduced values of 1.5–1.2 eV for the low-temperature oxidation of synthetic titanomagnetites ($\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$) under isothermal conditions. When their DTG data for $x = 0.2$, and $x = 1$ are analysed by method II the activation energies are 1.26 and 1.0 eV for temperatures up to 180°C , and 0.42, and 0.29 eV respectively for the range 180 – 280°C . To resolve this apparent discrepancy between the data, their isothermal plots of α against time for $x = 0.4$ were reanalysed by the methods of 'initial slope' and Rao and Rigaud (1975) which yielded 0.42 eV and 0.30 eV respectively. It is therefore concluded that the high values around 1.3 eV may be correct for the initial stage of oxidation, but that 0.35 eV may be more appropriate for the majority of the reaction.

During oxidation of the spinels, ferrous iron will diffuse towards the surface due to the oxygen potential gradient. At the surface, a compound rich in ferric iron will form, through which the ferrous iron must pass. In comparison with cation transport, oxygen diffusion is usually negligible, but with a large potential gradient it may become important.

During interdiffusion at a low oxygen partial pressure the situation is different since the iron moves under its own compositional gradient, and the potential gradients. The effective driving force for interdiffusion is much less than that for oxidation which results in a low activation energy and a relatively high diffusion coefficient for the latter.

A crude estimate of Fe^{2+} diffusion rates during oxidation may be gained from the isothermal TG data of Readman (1972). For material with $x = 0.4$, $t_{1/2}$, the times to reach $\alpha/2$, at 200, 220, 240, and 280 °C were 340, 88, 25, and 10 minutes respectively. Assuming no diffusion of oxygen, and an average grain size of 400 Å diameter, then an average diffusion distance of 50 Å is necessary to enable 50% oxidation by volume of each sphere. Employing the approximate solution to equation (1), $x^2 \approx 4Dt$, diffusion coefficients of $3 \times 10^{-10} \text{ cm}^2 \text{ sec}^{-1}$ to $1.04 \times 10^{-8} \text{ cm}^2 \text{ sec}^{-1}$ are obtained from 200 to 280 °C. These values are comparable with the fastest rates of interdiffusion at 1034 °C (fig. 5). A plot of $\ln D$ against $1/T$ is not linear, but yields 1.2 eV at the lower temperatures, and 0.52 eV at the higher temperatures, which agrees with most of the more rigorous analyses.

Conclusions

Diffusion of ferrous iron in the spinel structure is relevant to several problems of rock and mineral magnetism especially maghemitization and submarine weathering of titanomagnetites.

The interdiffusion experiments performed between the Fe^{2+} -bearing spinels and their magnesium counterparts showed that diffusion rates were composition dependent, but that Fe_2GeO_4 (all iron in *B* site) was associated with lower activation energy, and higher diffusion coefficient than FeAl_2O_4 (25% of iron in *B* site).

Oxidation kinetics of the spinels determined from non-isothermal TG data, analysed by six methods, gave results which were in broad agreement. During oxidation, diffusion of ferrous iron located at *B* sites may be identified with an activation energy of 0.27 (± 0.05) eV, and *A* site with 0.71 (± 0.09) eV. These results provide further support for the model of O'Reilly and Banerjee (1966) that *B* site Fe^{2+} iron will be more rapidly oxidized than *A* site Fe^{2+} .

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