

België 1, 57 (1961)] expressed doubts about homologies proposed by Patterson, but Mills's (1) functional studies essentially support the cusp homologies proposed by Patterson. In our paper we have adopted Patterson's cusp nomenclature.

5. G. G. Simpson, *Am. J. Sci.* **10**, 451 (1925).
6. ———, *Mem. Yale Peabody Mus.* **3**, (1929).
7. ———, *A Catalogue of the Mesozoic Mammalia in the Geological Department of the British Museum* (W. Clowes, London, 1928). Simpson placed *Tinodon* (on the basis of lower teeth and jaws only) in the Spalacotheriidae together with the British genera *Spalacotherium* and *Peralesstes*. He considered *Eurylambda* (on the basis of a crushed right maxilla with a single molar) to be a symmetrodont *incertae sedis*. He discussed the possibilities that *Eurylambda* may represent either an upper of *Amphidon* or of *Tinodon*, but he concluded that, in view of the doubtful character of the evidence, it was best to place it in a separate genus. Simpson figured the crown view of *Tinodon* (6) as having the three main molar cusps arranged in a symmetrical triangle; furthermore, he stated in *The Catalogue of the Mesozoic Mammalia* that *Tinodon* had molars more symmetrical than the British *Spalacotherium*. On the basis of the comparable asymmetry of the crowns of *Spalacotherium* and *Peralesstes*,

he concluded that they were probably upper and lower teeth of the same animal.

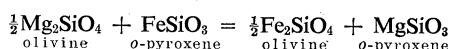
8. Patterson (4) divided the symmetrodonts into two distinct groups. One group, the "acute-angled" symmetrodonts, includes *Spalacotheroides*, *Spalacotherium* and *Peralesstes*. In these genera the three cusps of the trigon and trigonid form an angle of less than 90°. The second group includes forms with more open triangles, that is, *Eurylambda*, *Tinodon*, and *Manchurodon*. He considers the second group as more specialized than the acute-angled symmetrodonts and that members of this group tend toward the development of mesiodistal shear (for example, the triconodonts).
 9. B. Patterson, *Fieldiana Zool.* **37**, 689 (1955).
 10. W. A. Clemens, *Palaeontology* **6**, 55 (1963).
 11. B. Bohlin, *Bull. Geol. Inst. Univ. Upsala* **31**, 363 (1945), [as quoted by Patterson (4) in this regard].
 12. G. G. Simpson, *Palaeobiologica* **5**, 127 (1933), stated that jaw movements in symmetrodonts were strictly orthal, but Patterson (4, 9) cited oblique, parallel wear striations in *Spalacotheroides* as evidence of ectantal movement during jaw closure. We have observed similar features in *Tinodon lepidus* (U.S.N.M. 2131) and agree with Patterson's interpretation.
 13. Supported by an NSF grant.
- 10 October 1966

Equilibration Temperatures of Iron and Magnesium in Chondritic Meteorites

Abstract. The distribution coefficients for Fe^{++} and Mg^{++} were calculated from new microprobe analyses of coexisting olivine, orthopyroxene, and calcic pyroxene in chondritic meteorites. Interpretation of the data shows that (i) the equilibration temperatures were of the order of 850°C, and (ii) the olivine-orthopyroxene partition does not reflect ideal behavior. This equilibration temperature is much lower than previous estimates.

One of the major problems in meteoritics is determination of the temperatures represented by the partition of Fe^{++} and Mg^{++} among coexisting olivine, orthopyroxene, and calcic pyroxene in chondritic meteorites that have uniform silicate compositions. Previous studies of this problem (1, 2), which dealt only with the data on the partition of Fe^{++} and Mg^{++} between coexisting olivine and orthopyroxene, have arrived at temperatures of >900°C (1) and ~1250°C (2). On the basis of these temperatures some authors (3) have concluded that the Fe^{++} - Mg^{++} partition results from equilibrium crystallization of olivine and orthopyroxene at or near the liquidus, and have discounted the influence of metamorphism on the compositions of the silicates in chondrites. On the basis of evidence discussed below, one may now argue that the temperatures previously deduced are too high by as much as 400°C.

The use of the compositions of coexisting olivine and orthopyroxene for geothermometry depends upon the partitioning of Fe^{++} and Mg^{++} between these phases according to the reaction



The equilibrium constant for this reaction may be written

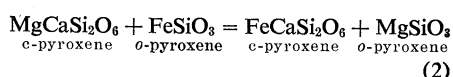
$$K_1 = [(\gamma_{Fe}^{OL} \cdot \gamma_{Mg}^{OPX}) / (\gamma_{Mg}^{OL} \cdot \gamma_{Fe}^{OPX})] \times [(X_{Fe}^{OL} \cdot X_{Mg}^{OPX}) / (X_{Mg}^{OL} \cdot X_{Fe}^{OPX})] \quad (1a)$$

where X_A^a denotes the mole fraction of element A in mineral a , and γ_A^a denotes the activity coefficient of element A in mineral a ; K_1 is dependent on P and T , and γ_A^a is dependent on P , T , and the composition of the mineral phase. In the special case where both mineral species are ideal solid solutions ($\gamma_A^a = 1$),

$$K_1 = Kd_1 = (X_{Fe}^{OL} \cdot X_{Mg}^{OPX}) / (X_{Mg}^{OL} \cdot X_{Fe}^{OPX}) \quad (1b)$$

where Kd_1 is the distribution coefficient determined from the compositions of the coexisting phases and assumed ideality.

A similar set of equations can be written for the mineral pair orthopyroxene-calcic pyroxene:



$$K_2 = [(\gamma_{Fe}^{Ca-PX} \cdot \gamma_{Mg}^{OPX}) / (\gamma_{Mg}^{Ca-PX} \cdot \gamma_{Fe}^{OPX})] \times [(X_{Fe}^{Ca-PX} \cdot X_{Mg}^{OPX}) / (X_{Mg}^{Ca-PX} \cdot X_{Fe}^{OPX})] \quad (2a)$$

and, on the assumption of ideality,

$$K_2 = Kd_2 = (X_{Fe}^{Ca-PX} \cdot X_{Mg}^{OPX}) / (X_{Mg}^{Ca-PX} \cdot X_{Fe}^{OPX}) \quad (2b)$$

The temperature dependence of K , at constant pressure, may be given by

$$\ln K = -\Delta G^\circ / RT \quad (3)$$

where ΔG° is the change in standard free energy for the reaction involved.

Both exchange reactions have been discussed in terms of terrestrial mineral assemblages by several authors, with the following results. (i) Attempts (4, 5) to demonstrate a simple relation between the compositions of coexisting olivine and orthopyroxene and rock type (for example, igneous versus metamorphic) have largely failed. Little, if any, evidence indicates that Eq. 1 represents partition between ideal solid solutions; rather, the evidence suggests that the partition relations for Eq. 1 are complex. (ii) Several authors (5-7) have shown that Eq. 2 *does* behave as though both mineral species were ideal solid solutions; furthermore, that one can separate high-temperature (igneous) rocks from moderate-temperature (metamorphic) rocks on the basis of their Fe^{++} - Mg^{++} partition as defined by Eq. 2b. The data from one such author (7) are presented in Fig. 1. The 45° lines show the curves obtained from Eq. 2b for $Kd = 0.54$ and 0.73.

Little usable data from experimental petrology exists for geothermometry by the above systems. Older data (8) have been used (1, 2) to obtain information for the olivine-orthopyroxene pair, but the data are much too imprecise to

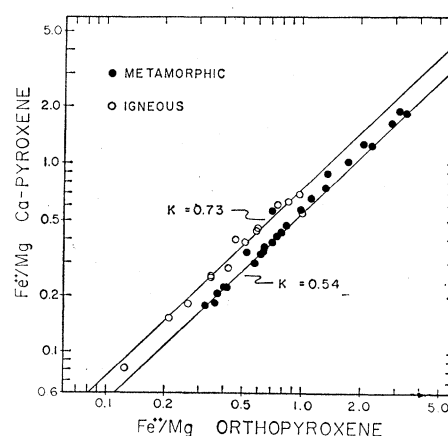


Fig. 1. Composition of coexisting orthopyroxene and calcic pyroxene from terrestrial rocks (7). The lines for $K = 0.54$ and 0.73 are for solutions of Eq. 2b: ideal solid-solution partition. The near-ideal behavior of this mineral pair in nature is illustrated by the nearly colinear plot of data points.

Table 1. Average mineral compositions in highly recrystallized ordinary chondrites. Numbers of chondrites averaged appear in parentheses (see Table 2). See text for minor constituents. For major constituents the spread of values about the average is within about 2 percent of the amount present. Abbreviations: Fa, Fe_2SiO_4 ; Fo, Mg_2SiO_4 (Fa + Fo, 100 mole percent); Fs, FeSiO_3 ; En, MgSiO_3 ; Wo, CaSiO_3 (Fs + En + Wo, 100 mole percent).

Group	Constituents (mole percent)							
	Olivine		Orthopyroxene			Calcic pyroxene		
	Fa	Fo	Fs	En	Wo	Fs	En	Wo
H (4)	19.2	80.8	16.8	81.7	1.5	6.1	48.8	45.1
L (9)	24.6	75.4	20.7	77.5	1.8	7.7	47.7	44.6
LL (8)	30.9	69.1	24.5	73.3	2.2	9.7	46.7	43.6

Table 2. Distribution coefficients of Fe^{++} and Mg^{++} for ordinary chondrites. Chondrite numbers: (H group) 1, Cedar, Kansas; 2, Estacado; 3, Guarena; 4, Oakley; (L group) 1, Bath Furnace; 2, Bruderheim; 3, Coon Butte; 4, Forksville; 5, Kyushu; 6, Langhalsen; 7, Leedey; 8, Modoc; 9, Ness County; (LL group) 1, Appley Bridge; 2, Benton; 3, Douar Mghila; 4, Ensishheim; 5, Jelica; 6, Manbhoom; 7, Mangwendi; 8, Varvik (Nas). Grand average (all groups), calcic pyroxene-orthopyroxene Kd_2 , 0.61 ± 0.02 .

Chondrite No.	Group					
	H		L		LL	
	Kd_1	Kd_2	Kd_1	Kd_2	Kd_1	Kd_2
1	1.16	0.60	1.21	0.59	1.36	0.60
2	1.18	0.64	1.24	0.58	1.36	0.64
3	1.16	0.61	1.19	0.63	1.32	0.65
4	1.14	0.59	1.25	0.63	1.34	0.61
5			1.23	0.62	1.35	0.65
6			1.20	0.61	1.37	0.63
7			1.19	0.55	1.34	0.60
8			1.25	0.61	1.28	0.60
9			1.25	0.60		
Averages (within 0.02)						
	1.16	0.61	1.22	0.60	1.34	0.62



Fig. 2. Recrystallized texture of one of the samples studied (Guarena, a type-6 H-group chondrite). Scale, 0.1 mm.

allow meaningful conclusions to be drawn. Recent data by Nafziger (9) are useful and will be referred to later. Virtually no experimental data are yet available for the partitioning of Fe^{++} and Mg^{++} between orthopyroxene and calcic pyroxene.

In the light of the above discussion, and with the new data presented below, one can now reexamine the problem of the Fe^{++} - Mg^{++} distribution in chondritic minerals, and the use of this relation for geothermometry.

We used the techniques of electron-probe microanalysis to determine the compositions of coexisting olivine, orthopyroxene, and calcic pyroxene in chondritic meteorites (10); several chondrites were selected from the three major groups of ordinary chondrites: H, L, and LL groups (11). Since most of the calcic pyroxene in ordinary chondrites results from recrystallization of fine-grained material, it can only be located with ease in chondrites that are strongly recrystallized (type-6 chondrites; 12): most chondrule outlines are indistinct or nearly obliterated and the textures (Fig. 2) are largely xenoblastic, with readily recognizable plagioclase.

The data are summarized (13) in Tables 1 and 2 and in Fig. 3; the data in Table 1 are normalized to 100 mole percent of the Fe, Mg, and Ca end-member minerals. The minor constituents for each mineral are as follows (mole percentages): (olivine) Mn_2SiO_4 , 0.5; (orthopyroxene) MnSiO_3 , 0.5, and $\text{NaCrSi}_2\text{O}_6$ (14), 0.5; (calcic pyroxene) MnSiO_3 , 0.4, and $\text{NaCrSi}_2\text{O}_6$ (14), 3.5. Aluminum is present in only trace amounts, reaching an Al:Si (atomic) ratio of 0.01 in the calcic pyroxene, as a maximum. The presence of these minor constituents does not significantly affect the considerations based on Fe^{++} and Mg^{++} .

The most important relation shown by the data is that the value of Kd for calcic pyroxene-orthopyroxene (Kd_2) is essentially independent of the group to which a chondrite belongs; this is in direct contrast with the relation for Kd_1 (olivine-orthopyroxene). In view of the observational evidence from coexisting terrestrial olivine-orthopyroxene and calcic pyroxene-orthopyroxene, this relation is interpreted as showing that: (i) the Fe^{++} - Mg^{++} partition in all three groups of ordinary chondrites was established at essentially the same temperature, and (ii) the Fe^{++} - Mg^{++} partition in the system olivine-orthopyroxene depends on composition as well as temperature and pressure (15). This latter

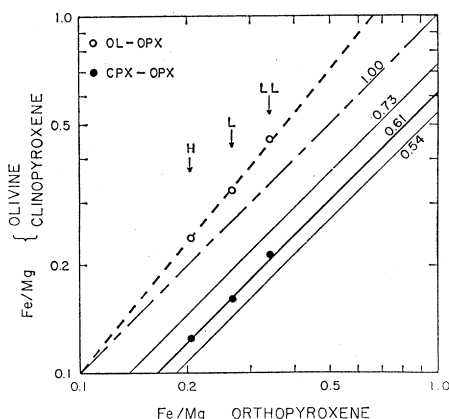


Fig. 3. A plot for the average compositions of the chondrites studied. The curves for $K = 0.54$ and 0.73 (Fig. 1) represent ideal behavior. The curve for $K = 0.61$, shown for the data on orthopyroxene-calcic pyroxene (clinopyroxene), was plotted on the assumption of ideality. One can see that the olivine-orthopyroxene points do not define a curve representing ideal behavior, but show instead a compositional dependence for the partition function.

conclusion is confirmed by the recent work of Nafziger (9) on the system $\text{SiO}_2\text{-FeO-MgO}$, which demonstrates that the olivine solid solution is distinctly less ideal than the orthopyroxene solid solution, and that the assumption that $K_1 \approx Kd_1$ is thus not valid. Any inferences of temperature based on this assumption (1, 2) are open to serious criticism.

The true temperature represented by Kd_2 for the chondrites may be estimated from the work of Bartholomé (5) and Kretz (7); they estimated the temperatures corresponding to various terrestrial Kd_2 's and thus determined the temperature dependence of K versus T . This relation is shown in Fig. 4 for the data of Kretz (7), although Bartholomé's data are essentially the same.

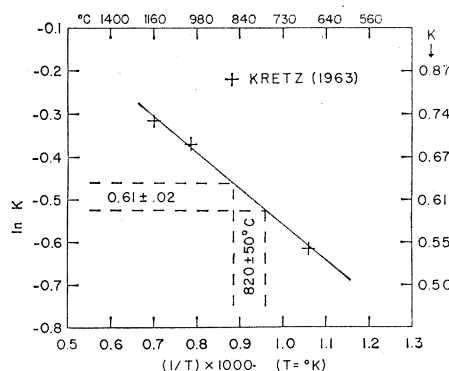


Fig. 4. Estimated dependence of Kd_2 versus temperature (7). The chondrite partition for orthopyroxene-calcic pyroxene corresponds to a temperature of $820 \pm 50^\circ\text{C}$.

From Fig. 4 the temperature represented by the chondritic $\text{Fe}^{++}\text{-Mg}^{++}$ partition between orthopyroxene and calcic pyroxene may be estimated at $820 \pm 50^\circ\text{C}$ (16). This value is 400°C lower than Craig's (2), and distinctly lower than the temperatures implied by Mueller (1). In view of the demonstrated nonideality of the olivine-orthopyroxene system (9), the demonstrated near-ideal behavior of the orthopyroxene-calcic pyroxene system (5-7), and the lack of reliable K -versus- T data for olivine-orthopyroxene, this lower estimate is considered much more realistic.

This temperature of $\sim 800^\circ\text{C}$ must be interpreted cautiously; it is not considered to represent the maximum temperatures experienced by the ordinary chondrites, nor does it represent the true crystallization temperature of the minerals implicated; it is interpreted as the lowest temperature at which Fe^{++} and Mg^{++} ions possess sufficient mobility to effect equilibration among phases. For a strongly recrystallized chondrite, therefore, the values of Kd obtained may reflect *retrograde equilibration* that was occurring during cooling of the chondrite from higher metamorphic temperatures. This conclusion is supported by the report of $Kd_2 = 0.61$ for coexisting orthopyroxene and calcic pyroxene from silicate nodules in the Odessa iron meteorite by Marshall and Keil (17); they also concluded that the corresponding temperature of $\sim 800^\circ\text{C}$ represents the temperature below which $\text{Fe}^{++}\text{-Mg}^{++}$ exchange became insignificant, since the iron-nickel of that meteorite must have once been molten.

As a consequence of these conclusions, the fact that less-metamorphosed chondrites (for example, type 4; 12) such as Bjurböle have the same $\text{Fe}^{++}\text{-Mg}^{++}$ relations between their olivine and Ca-poor pyroxene as do highly metamorphosed (type 6) chondrites, such as Leedey or Bruderheim, is easily explained: the mineral compositions in Bjurböle are the result of metamorphic heating to a temperature of $\sim 800^\circ\text{C}$ for sufficient time to allow the olivine and Ca-poor pyroxene to establish uniform compositions (one assumes that the minerals in Bjurböle were of variable composition prior to any metamorphic heating; 18) and to establish an equilibrium partition. At this temperature little textural recrystallization occurred except in the finest-grained portions of the chondrite. On the other hand, the compositions of the minerals in well-recrystallized chondrites were also established at $\sim 800^\circ\text{C}$, but repre-

sent equilibrium that was continually adjusting to lowering temperatures from the maximum (perhaps 1000° to 1200°C) reached during metamorphism.

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9. R. H. Nafziger, thesis, Pennsylvania State Univ., 1966.
10. In the laboratories of Advanced Metals Research Corp., Burlington, Mass. An instrument similar to the Philips AMR/3 microprobe was employed; analyzed minerals were used as standards. The data were taken at 20-kv accelerating voltage and $\sim 0.2\text{-}\mu$ a specimen current. The techniques employed will be described later.
11. According to the nomenclature proposed by K. Keil and K. Fredriksson, *J. Geophys. Res.* **69**, 3487 (1964).
12. According to the petrologic subdivisions developed by W. R. Van Schmus and J. A. Wood, *Geochim. Cosmochim. Acta*, in press. Type 6 represents the most-recrystallized chondritic meteorites.
13. More detailed data will be presented later. The average deviations of individual samples (Table 1) are within 2 percent of the average values for the major constituents; some deviations probably reflect true differences, but much of the scatter may reflect analytical imprecision. True analytical precision has not yet been measured by multiple analyses of the same sample, but it is estimated at ± 3 percent of the amount present. The scatter of Kd values within each group in Table 2 is comparable to errors in analytical precision for individual analyses.
14. A semiquantitative check for Na has been performed on only one sample (Estacado), but the results suggest that the chromium present in the pyroxene minerals may be represented by the ureyte end-member $\text{NaCrSi}_2\text{O}_6$ [C. Frondel and C. Klein, Jr., *Science* **149**, 742 (1965)].
15. It is assumed that Fe^{++} and Mg^{++} diffusion rates in olivine are comparable to or greater than those in pyroxene; this assumption is considered valid.
16. The $\pm 50^\circ\text{C}$ represents only the uncertainty in temperature due to uncertainty in Kd_2 . The additional uncertainty, due to the uncertainty of the correlation of Kd_2 versus T , may be as great as $\pm 100^\circ\text{C}$; its resolution requires experimental data.
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21. We thank R. T. Dodd and L. S. Walter for comments on the manuscript. Samples were provided through the courtesy of C. B. Moore (Nininger Collection, Arizona State Univ.) and K. Fredriksson (U.S. National Museum).

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