The olivine, pyroxene, and metal content of chondritic meteorites as a consequence of Prior's rule

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Summary. There is an important corollary to Prior's rule to the effect that as the state of oxidation of meteorites is increased the quantity of olivine increases relative to pyroxene and metallic iron. We have derived a rigorous parametric expression for this corollary and find that, as in the case of the quantitative interpretation of the rule itself, there is in this case also a fair correspondence to the observational data, so that the validity of the rule is further supported.

ONE of the most useful integrating concepts of meteoritics was proposed by Prior (1916) in the form of his now famous rule, which states that: The less the amount of nickel-iron in chondritic stones, the richer it is in nickel and the richer in iron are the magnesium silicates. It is convenient to think of the rule as consisting of two parts, the one relating the total quantities of reduced and oxidized iron to each other and the other relating the compositions of the silicate and metallic phases.

Although the original statement of Prior's rule contains no particular implication of a quantitative relation, a strict interpretation of the rule is possible in terms of well-defined states. The strict interpretation referred to is the univariant oxidation or reduction of the meteorites at fixed composition with respect to the major chemical constituents Mg, Fe, Si, and Ni so that only the quantity of oxygen is subject to variation.

The quantitative form of that part of Prior's rule that relates the total quantities of oxidized and reduced iron was first given by Urey and Craig (1953) in their extensive survey of the compositional variations among the chondritic meteorites. If the bulk composition other than oxygen is held constant as stated above, progressive oxidation or reduction yields a straight line of negative slope when the reduced iron is plotted against oxidized iron. When, however, Urey and Craig plotted the existing chemical analyses on this diagram they found only a rough quantitative agreement and further noted that the data points fell in two groups one on either side of the line so that a deficiency of total iron distinguished one group from another. These two groups, which were called the high- and low-iron groups, have also come to play an important part in the literature of meteoritics.[1]

Some time later Ringwood (1961) made a study of the second part of Prior's rule, which deals with the relation between the compositions of the silicate and metallic phases, and found that the data could be approximated by a highly distinctive curve. Subsequently, an analytical derivation of this relation was provided (Mueller, 1963). The relation yielded a family of curves similar to the empirical curve in which each curve corresponded to different Mg, Si, Ni, etc. contents. Consequently, if all the chondritic meteorites obeyed Prior's rule exactly the compositions of the silicate and metal phases should be representable by a single one of these curves. But it was found that again only a rough semiquantitative correspondence with the data of Ringwood was possible. However, it is of considerable significance that the analytical relation yields curves of the same distinctive form as the observational data.

The phase content of meteorites as a consequence of Prior's rule

In addition to the variations in reduced and oxidized iron and phase compositions that form the explicit statement of Prior's rule there is at least one other interesting consequence of the rule. This is the implicit variation in the relative quantities of the phases olivine, pyroxene, and metal within the sequence of types defined by the rule.

Elsewhere (Mueller, 1963) it was shown that the fundamental reactions involved here are:

$$\underset{\text{olivine}}{\tfrac{1}{2}Mg_2SiO_4}+\underset{\text{pyroxene}}{FeSiO_3} \rightleftharpoons \underset{\text{olivine}}{\tfrac{1}{2}Fe_2SiO_4}+\underset{\text{pyroxene}}{MgSiO_3}, \qquad (a)$$

$$\underset{\text{pyroxene}}{2MgSiO_3}+\underset{\text{metal}}{2Fe}+\underset{\text{gas}}{O_2} \rightleftharpoons \underset{\text{olivine}}{Mg_2SiO_4}+\underset{\text{olivine}}{Fe_2SiO_4}, \qquad (b)$$

$$\underset{\text{pyroxene}}{FeSiO_3}+\underset{\text{metal}}{Fe}+\underset{\text{gas}}{\tfrac{1}{2}O_2} \rightleftharpoons \underset{\text{olivine}}{Fe_2SiO_4}. \qquad (c)$$

In our present state of knowledge of the constituents that enter into these reactions it may be assumed that all the silicate phases form ideal

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[1] The grouping into high- and low-iron groups appears to be identical with that into olivine-bronzite and olivine-hypersthene chondrites.

solutions of their magnesium and iron end-members (Mueller, 1964). Even if these solutions do not exhibit ideal behaviour this will not affect the end-results we seek here. However, if ideality may be assumed, we may write the following expressions for the equilibrium constants corresponding to the three reactions:

$$K_a = X^{\text{px}}_{\text{Mg}}(1-X^{\text{ol}}_{\text{Mg}})/X^{\text{ol}}_{\text{Mg}}(1-X^{\text{px}}_{\text{Mg}}), \tag{1}$$

$$K_b = (X^{\text{ol}}_{\text{Mg}})^2(1-X^{\text{ol}}_{\text{Mg}})^2/(X^{\text{px}}_{\text{Mg}})^2(a^M_{\text{Fe}})^2P_{\text{O}_2}, \tag{2}$$

$$K_c = (1-X^{\text{ol}}_{\text{Mg}})^2/(1-X^{\text{px}}_{\text{Mg}})a^M_{\text{Fe}}P^{\frac{1}{2}}_{\text{O}_2}. \tag{3}$$

In these expressions the X_{Mg}'s refer to the atomic fraction $\text{Mg}/(\text{Mg}+\text{Fe}^{2+})$ in the phase indicated by the superscript, P_{O_2} to the oxygen fugacity, and a^M_{Fe} to the activity of iron in the metallic phase. If we let

$$X^M_{\text{Fe}} = \text{Fe}/(\text{Fe}+\text{Ni})$$

in the latter phase we may write: $a^M_{\text{Fe}} = X^M_{\text{Fe}}f^M_{\text{Fe}}$, where f^M_{Fe} is the activity coefficient of iron in the metallic phase. Although we do not know f^M_{Fe} precisely it probably does not vary greatly from unity for either taenite or kamacite (Kubaschewski and Evans, 1958). However, regardless of the behaviour of f^M_{Fe} we know that the ratio $(1-X^{\text{ol}}_{\text{Mg}})/X^M_{\text{Fe}}$ must increase with increasing P_{O_2} since metallic iron is progressively oxidized to the ferrous iron of the silicates. To see this we may examine equation (3). Since K_a is close to unity for nearly all meteorites (Mueller, 1964), $(1-X^{\text{ol}}_{\text{Mg}}) \approx (1-X^{\text{px}}_{\text{Mg}})$ and (3) may be written as:

$$P^{\frac{1}{2}}_{\text{O}_2}K_c f^M_{\text{Fe}} = X^{\text{ol}}_{\text{Fe}}/X^M_{\text{Fe}},$$

so that the ratio $X^{\text{ol}}_{\text{Fe}}/X^M_{\text{Fe}}$ is a monotonic function of P_{O_2} at constant temperature. The same result also follows from equation (2). If now we define the ratio $X^S_{\text{Fe}} = \text{Fe}^{2+}/(\text{Mg}+\text{Fe}^{2+})$ for the silicates as a whole, we may say, because of the distribution relation (1), that the ratio $X^S_{\text{Fe}}/X^M_{\text{Fe}}$ behaves in the same way as $X^{\text{ol}}_{\text{Fe}}/X^M_{\text{Fe}}$. Consequently we define this ratio as: $R = X^S_{\text{Fe}}/X^M_{\text{Fe}}$. Also we define the normative mole fraction of the olivine phase as

$$L = \frac{\text{moles (Mg, Fe)}_2\text{SiO}_4}{\text{moles (Mg, Fe)}_2\text{SiO}_4+\text{moles (Mg, Fe)SiO}_3+\text{moles metallic Fe}}.$$

To obtain the relation between R and L we combine the reactions (*b*) and (*c*) to give the general oxidation reaction

$$\underset{\text{pyroxene}}{\text{(Mg, Fe)SiO}_3}+\underset{\text{metal}}{\text{Fe}}+\underset{\text{gas}}{\tfrac{1}{2}\text{O}_2} \rightarrow \underset{\text{olivine}}{\text{(Mg, Fe)}_2\text{SiO}_4}.$$

We now define the 'extent' of this reaction as α, the number of moles of reacted pyroxene and metallic iron. If we look at the reaction from the standpoint of oxidation as indicated by the arrow, then at the start of the process there will be px° moles of pyroxene of composition $MgSiO_3$ and Fe° moles of iron in combination with the Ni. Also if there is any olivine initially present this will be pure Mg_2SiO_4 and we may designate its molar quantity as ol°. Then since each reacted mole of pyroxene and iron produced one mole of olivine we obtain the following expressions[1] for R and L in terms of α, the extent of the reaction:

$$R = \alpha\{(\mathrm{Fe}^{\circ}-\alpha)+\mathrm{Ni}\}/(\mathrm{Fe}^{\circ}-\alpha)(\mathrm{px}^{\circ}+2\mathrm{ol}^{\circ}+\alpha)$$

$$L = (\mathrm{ol}^{\circ}+\alpha)/(\mathrm{px}^{\circ}+\mathrm{ol}^{\circ}+\mathrm{Fe}^{\circ}-\alpha),$$

If we now eliminate α from these expressions we obtain L as an explicit function of R in which ol°, px°, Fe°, and Ni may be varied as parameters to yield a family of curves. These curves may then be compared with values of R and L calculated from meteorite chemical analyses.

However, it is interesting first to consider the oxidation of a hypothetical 'pure enstatite chondrite' for which $\mathrm{ol}^{\circ} = 0$. The oxidation path (curve (1), fig. 1) then begins at the origin, traces a sigmoidal course, and approaches $L = 1$ asymptotically if $\alpha \rightarrow \mathrm{Fe}^{\circ} = \mathrm{px}^{\circ}$. However, it must be remembered that real enstatite chondrites would not follow precisely this path since they usually have a small excess of SiO_2 over $MgSiO_3$.

An oxidation path with more realistic values of the parameters is shown as curve (2) in fig. 1. Also shown are plotted values of L and R from 50 ordinary chondrites, computed from analyses given in the literature (table I). Although there is considerable scatter in these points it is apparent that there is at least an approximation to the strictly quantitative interpretation of Prior's rule.

The scatter shown by the points in fig. 1 has several sources. One source is undoubtedly errors in the chemical analyses. As pointed out by Keil and Fredriksson (1964), there are some large discrepancies between the fraction $Fe^{2+}/(Mg+Fe^{2+})$ as calculated from the bulk chemical analyses and the same quantity as determined from electron-microprobe measurements of the individual silicate compositions. This is true, for example, of the two points representing Collescipoli and Djati-Pengilon, which lie farthest from curve (2) in the lower part of the diagram.

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[1] In terms of Niggli type norms (per cation) L takes the form

$$L = 3(\alpha+\mathrm{ol}^{\circ})/(3\mathrm{ol}^{\circ}+\mathrm{Fe}^{\circ}+2\mathrm{px}^{\circ}).$$

Another source of scatter is, however, simply the failure of strict adherence to Prior's rule as already noted from the previous tests. It may, for example, arise from variation in the ratio Si/(Mg+Fe) (expressed as ol°). However, if it is kept in mind that Prior's rule is, in any event, of a statistical nature such scatter is always to be expected.

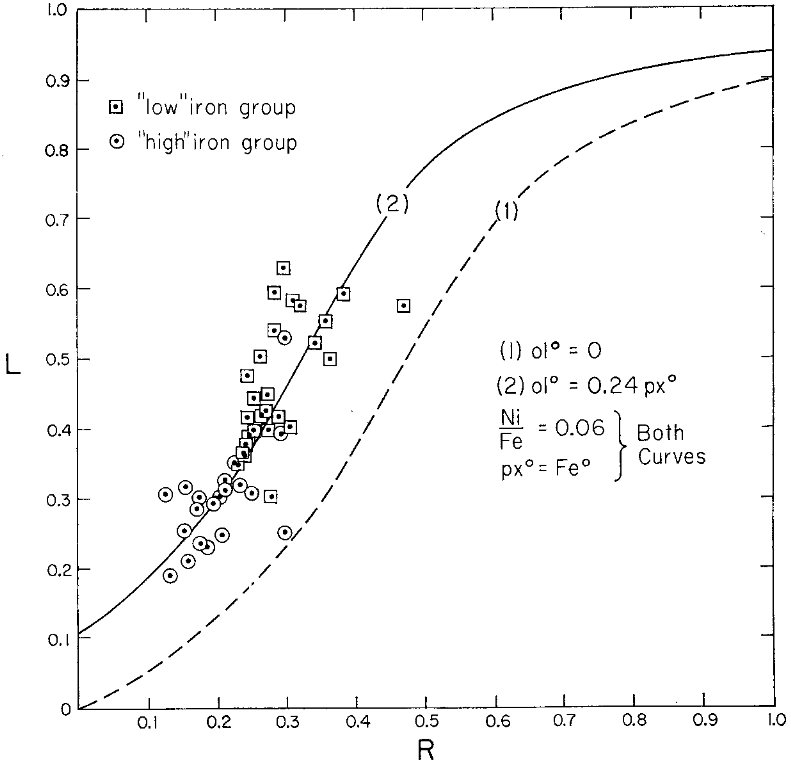

FIG. 1. Molecular normative olivine content, *L*, of 50 chondrites plotted against the ratio of oxidized to reduced iron, *R*. The curves are theoretical. 'Low' iron group refers to hypersthene chondrites and amphoterites; 'high' iron group refers to bronzite chondrites.

General conclusions

We see then that the two parts of the original statement of Prior's rule and its corollary regarding the normative phase content are adhered to in a semiquantitative way, while the strict quantitative interpretation yields several types of distinctive curves, which serve as a useful basis of comparison for the observational data.

TABLE I. Normalized mole fractions of bulk compositions, normative olivine (*L*), and ratio of oxidized to reduced iron (*R*) for 50 ordinary chondrites. The normalized mole fractions result from the subtraction from the original analyses of quantities of oxides corresponding to normative albite, anorthite, orthoclase, wollastonite, chromite, ilmenite, and whitlockite

		Bulk Mole Fraction					
Name	Type	MgO	FeO	SiO_2	*L*	*R*	Ref.
Albareto*	L	0·4716	0·1625	0·3659	0·631	0·296	1
Allegan*	H	0·4848	0·1009	0·4143	0·231	0·186	1
Barwell*	L	0·4658	0·1405	0·3937	0·446	0·272	10
Beaver Creek*	H	0·4677	0·1103	0·4219	0·248	0·206	1
Bjurböle	L	0·4798	0·1329	0·3873	0·476	0·243	1
Breitscheid*	H	0·5154	0·0863	0·3984	0·318	0·154	2
Bruderheim*	L	0·4619	0·1421	0·3960	0·427	0·272	3
Chantonnay*	L	0·4790	0·1554	0·3656	0·595	0·285	1
Château Renard*	L	0·4749	0·1289	0·3962	0·417	0·243	4
Collescipoli*	H	0·5348	0·0704	0·3948	0·308	0·125	1
Coon Butte*	L	0·4369	0·1406	0·4225	0·302	0·279	1
Dalgety Downs	L	0·4713	0·1298	0·3988	0·388	0·247	11
Djati-Pengilon*	H	0·4302	0·1566	0·4132	0·251	0·298	1
Ekeby*	H	0·4874	0·1249	0·3877	0·351	0·224	1
Estacado*	H	0·4583	0·1354	0·4062	0·306	0·250	4
Farmington*	L	0·4498	0·1496	0·4007	0·416	0·289	5
Forest City*	H	0·5013	0·0947	0·4040	0·286	0·169	1
Forksville	L	0·4515	0·1789	0·3696	0·577	0·321	1
Ghubara	H	0·4620	0·1575	0·3805	0·532	0·298	11
Hamlet	L	0·4462	0·1690	0·3848	0·554	0·357	5
Hessle*	H	0·4764	0·1250	0·3986	0·320	0·233	1
Hökmark*	L	0·4449	0·1658	0·3893	0·361	0·239	5
Holbrook*	L	0·4684	0·1218	0·4097	0·364	0·236	5
Homestead*	L	0·4698	0·1300	0·4002	0·376	0·242	1
Kasamatsu	H	0·5048	0·0964	0·3988	0·303	0·175	6
Kesen*	H	0·4916	0·1093	0·3991	0·292	0·197	7
Knyahinya*	L	0·4498	0·1612	0·3889	0·521	0·341	4
Kyushu*	L	0·4438	0·1520	0·4042	0·402	0·307	5
Merua*	H	0·4894	0·0832	0·4273	0·211	0·159	1
Mezö-Madaras*	L	0·4737	0·1533	0·3730	0·545	0·279	11
Mino	L	0·4747	0·1352	0·3901	0·444	0·253	7
Mocs*	L	0·4700	0·1194	0·4106	0·346	0·230	4
New Concord*	L	0·4731	0·1203	0·4065	0·368	0·232	4
Oakley*	H	0·4857	0·1143	0·4000	0·326	0·212	1
Ochansk*	H	0·5052	0·0835	0·4113	0·253	0·153	5
Ohuma†	L	0·4558	0·1416	0·4026	0·401	0·278	10
Ottawa	L	0·4448	0·1763	0·3790	0·593	0·384	4
Putinga	L	0·4432	0·1628	0·3939	0·582	0·315	11
Richardton*	H	0·4874	0·1173	0·3953	0·312	0·210	4
Rose City	H	0·5136	0·0715	0·4148	0·191	0·132	5
Sasagase	H	0·4862	0·1073	0·4064	0·292	0·197	8
Soko-Banja*	L	0·4395	0·1681	0·3924	0·500	0·364	1
Sone	H	0·4891	0·1153	0·3956	0·329	0·210	6
Ställdalen*	H	0·4877	0·0935	0·4188	0·235	0·175	1

TABLE 1 (*continued*)

Name	Type	Bulk Mole Fraction MgO	FeO	SiO_2	*L*	*R*	Ref.
St. Michel	L	0·4776	0·1434	0·3790	0·504	0·263	1
Tomhannock Creek*	H	0·4506	0·1559	0·3935	0·394	0·293	5
Tomita	L	0·4705	0·1333	0·3962	0·399	0·251	6
Vårvik*	L	0·4380	0·1765	0·3855	0·576	0·472	5
Wold Cottage†	L	0·4657	0·1410	0·3933	0·424	0·266	10
Yonozu	H	0·4878	0·1114	0·4008	0·304	0·204	9

* Electron-probe analyses of olivine and pyroxene in these chondrites have been made (Keil and Fredriksson, 1964; S. J. B. Reed in Moss, Hey, Elliott, and Easton, 1967).

† Separate chemical analyses of olivine and pyroxene in these chondrites have been made (Moss, Hey, Elliott, and Easton, 1967).

References. 1, Urey and Craig, 1953; 2, Vilcsek, 1959; 3, Duke *et al.*, 1961; 4, Mason and Wiik, 1961, 1963; 5, Wiik, 1956, 1965; 6, Miyashiro *et al.*, 1963*a*, 1963*b*, 1963*c*; 7, Miyashiro, 1962*a*, 1962*b*; 8, Murayama *et al.*, 1962; 9, Mason, 1963; 10, Moss *et al.*, 1967; 11, A. A. Moss anal., in Hey, 1967.

In the past it has sometimes been assumed that the sequence of meteorite oxidation types is also an evolutionary sequence in which perhaps the most highly reduced meteorites were derived in some way from a highly oxidized ancestor or vice versa. Prior himself believed that the sequence of types could be traced back to a parent magma of varying oxidation state. However, neither the evolutionary nor the magmatic concept is required to explain the observations. For example, precisely the same result might be obtained by the simultaneous crystallization from a vapour at subsolidus temperatures of the different members of the sequence if the vapour is assumed to exist in different oxidation states in different regions.

Actually, however, there exists a considerable body of evidence that seems to imply that the sequence of oxidation states has been derived at least in part by a reduction process beginning with material resembling the Class I carbonaceous chondrites, as has been stressed for some time by Ringwood (1961, 1966). This of course implies a track from right to left on the curves of fig. 1. According to Ringwood the ferrous iron of the silicates and other minerals was progressively reduced by carbon compounds such as free carbon and hydrocarbons with intervention of a liquid phase only at the highest attained temperatures.

Even the rather crude correspondence to Prior's rule, however, speaks impressively of the great homogeneity of the chondritic meteorites and certainly both its qualitative and quantitative aspects must be accommodated in any theory of their origin.

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