Oxygen and carbon isotopes were determined in the carbonate of the total sample and in a dolomite concentrate obtained by leaching out the calcite with 5-percent acetic acid. Acetic acid leaching does not introduce isotopic exchange. The isotopic values relative to the PDB-I standard are given in Table 2. Independent determination of the calcite and dolomite values by the phosphoric acid double-extraction method (*7*) could not be used because the reaction rates of calcite and high-calcium dolomite are almost identical. Therefore, the δO^{18} and δC^{13} (*8*) of the calcite were estimated by calculation using the x-ray diffraction result which indicated equal amounts of dolomite and calcite. When calcite is dissolved with acetic acid considerable dolomite is dissolved. If the original sample contained a spectrum of dolomites whose reactivity to acid is correlated with isotopic variations, then the dolomite isotopic composition in Table 2 would be that of the least reactive dolomite, and the calculated calcite isotopic composition would be in error.

The values for calcite and dolomite, though similar, are significantly different. These differences may or may not be real. Sharma and Clayton (*9*) have shown that the δO^{18} values of ideal dolomites should be corrected by subtracting 0.8 per mille to account for a difference in behavior of dolomite and calcite when prepared by the phosphoric acid method. However, O'Neil (*10*) has shown that this correction does not apply when dealing with high-calcium dolomites.

If we apply the oxygen isotope paleotemperature equation (*11*) to the calcite data (assuming a water δO^{18} of 0.0 per mille), we get a temperature of $-0.3°C$. Present-day water temperatures at the locality are about 5°C. Experimental data (*7, 12*) and studies of hydrothermal dolomite (*13*) suggest that dolomite may concentrate O^{18} relative to calcite by as much as 7 per mille at 25°C. This would allow a calculated isotopic temperature as high as 20°C for the dolomite. However, most synsedimentary pairs of dolomite and calcite which are presumed to have formed at earth surface temperatures do not exhibit the predicted difference in oxygen isotope composition. This observation has led some workers to conclude that such dolomites form without establishing isotopic equilibrium (*14*).

The δC^{13} values of -35.1 and -41.0 are very unusual. Recent carbonate sediments have δC^{13} values ranging from 2.0 to -3.0 per mille (*15*), although individual sediment contributors can have values as negative as -8.0 per mille (*16*). Ancient marine limestones range from 2.0 to -6.0 per mille and rarely have values as negative as -12.0 per mille (*17*). The only carbonate values which are as negative as the material studied here are samples of calcite from the cap rock of salt domes (*18*). Cap rock calcite is believed to originate as a by-product of sulfate reduction by bacteria. The origin of the carbonate carbon is CO_2 derived from the oxidation of the petroleum hydrocarbons which serve as a source of energy for the bacteria. The fact that petroleum is depleted greatly in C^{13} (δC^{13} from -15 to -35 per mille) and the fact that C^{12} atoms are selectively metabolized by the bacteria account for the highly negative C^{13} values (C^{13} from -25 to -55 per mille) found in the cap rock calcite (*18*). Among possible sources of the carbon in the Oregon carbonates, only petroleum and natural gas have sufficiently light carbon isotope ratios. However, it is possible that some combination of a nonhydrocarbon source of light carbon and bacterial selectivity during oxidation might have produced the unusually light carbon in this material. If the carbonate formed from a source of carbon other than normal seawater, the absence of C^{14} activity may not be an indication of age. If a bacterial metabolic process was involved in the formation of the calcite and dolomite, then the oxygen isotope data may indicate nonequilibrium conditions and have no paleotemperature significance.

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Superconductivity and the d-Shell

Abstract. *The various isotope effects on the superconducting transition temperature of* Mo_2B *and* W_2B *have been measured. Together with resistivity data they indicate that the* d*-shell forms a highly stable electron configuration for molybdenum and tungsten. This leads to an understanding of high superconducting transition temperatures.*

We have experimental evidence from isotope effects and normal state resistivities that tungsten, though being a transition element, behaves essentially like a nontransition element with respect to superconductivity, that is, the *d* electrons do not substantially take part in the phenomenon. The resulting conclusion, to consider the superconductivity of W as that of a nontransition element, seems at first rather surprising. A closer look, however, shows this to be not only quite reasonable but also gives a simple explanation for the superconducting behavior of the transition elements.

The isotope effect on the superconducting transition temperature T_c is distinguished by the typical differences between the superconducting behavior of the transition elements and the nontransition elements. This difference is due to their electron configuration, namely, *sd* in the transition series and *sp* in the others.

The T_c of W is the lowest of any element known, and to determine the isotope effect of tungsten itself would be an extremely difficult experiment. It requires measuring a shift in transition temperature amounting, at the maximum, to less than 0.2 millidegree. We have therefore tried to look for this isotope effect in an indirect way. We measured the isotope effects in Mo_2B, $T_c = 5.85°K$, and in W_2B, $T_c = 3.18°K$. These compounds have isomorphous body-centered tetragonal crystal structures with nearly identical lattice parameters. In each case the isotopic mass of one of the constituent elements was varied with the naturally occurring mass for the other. The isotopes used were:

Mo	92	94	96	98	100
W	182	183	184	186	
B	10	11			

along with the naturally occurring elements. The results (*1*) obtained are shown in Table 1.

The extremely large isotope effect of B in W_2B, versus a negligible effect in Mo_2B, indicates a W-B interaction larger than that of Mo-B. This is also reflected in the greater stability of W_2B, which melts congruently at 2800°C, while Mo_2B decomposes peritectically at 2000°C. Since the boron isotope effect involves optical phonons as well, let us not consider it for now. More suggestive at present, though, are the results for variation of the heavy masses.

Table 1. Isotope effect on the superconducting transition temperature, T_C, in the compounds Mo_2M and W_2B. The number α is obtained from fitting the data to the relation $T_C \sim M^\alpha$, where M is the mass of the heavy element. The errors quoted are a measure of the scatter of the data.

Compound	Mass varied	$\Delta T_c/\Delta M$ °K/Mass Unit	α
Mo_2B	Mo	-0.025 ± 0.0014	-0.42 ± 0.02
Mo_2B	B	-0.002 ± 0.008	
W_2B	W	-0.009 ± 0.001	-0.52 ± 0.05
W_2B	B	-0.028 ± 0.005	

These results were fitted to the relation $T_c \sim M^\alpha$, where we let M be the mass of the heavy atom only, and are shown in Table 1. Comparing this to the results found for pure Mo $\alpha = -0.33$ (*2*), we obtain by direct proportionality for pure W an $\alpha = -0.41$. Although the analogy between Mo and W, on the one hand, and Mo_2B and W_2B on the other, undoubtedly cannot be drawn this simply, nevertheless it seems likely that α for W is higher than for Mo; α is generally close to -0.5 in the nontransition element superconductors and is always lower in the transition elements. Since deviations from -0.5 must therefore be due to *d* electron involvement, we conclude that in W metal the *d*-shell is particularly stable and, for that reason, only weakly interacting with the *s* electrons.

This stability apparently arises from two causes, one, the lowering of energy due to filling a half *d*-shell and, two, from the high lattice stability obtained for a d^5s^1 configuration, as exists for the elements in column VI in a bcc crystal lattice (*3*). This can be deduced from the heat of atomization (*4*) in this part of the periodic table (see Table 2). The maximum in cohesive energy is at W in the third long period but is between Nb and Mo in the second. Thus the *d*-shell, being responsible for bonding, is in a most stable configuration at these places. Just at these places of maximum stability there is now a minimum in T_c. For Mo-Nb alloys this occurs at about $Nb_{.3}Mo_{.7}$ with a transition temperature of 16 millidegrees (*5*), and for the third long period the minimum seems to be very close to W, which has a T_c of about 12 millidegrees (*6*).

From the normal state resistivity, there is further evidence that the *d*-shell is particularly stable in W and to a great extent also in Mo. These resistivity data for the normal state also indicate that the electronic behavior of W and Mo is strikingly different from that of Nb. At temperatures lower than about 1/10 the Debye temperature, three types of temperature-dependent resistivities occur. One is a quadratic dependence due to electron-electron and electron spin wave scattering (*7*). This term is dominant in Mn and has possibly been seen in some other transition metals at very low temperatures. However, it will not be considered in the following discussion.

The other two terms are T^3 and T^5. Their occurrence (*8–11*) throughout the transition elements is given in Table 2. Wilson has shown (*12*) that a cubic dependence will arise for the process of a conduction electron being scattered by a phonon into a *d*-band. In the *d*-band, where electrons are considered to have a much higher effective mass, they will not participate in the conduction process. The most frequently occurring term, T^5, has been explained by Bloch (*13*). Physically it arises from the conduction of *s* electrons being scattered by phonons. This process results in a net loss of electron momentum along the current direction.

Recently prepared Nb of ultra high purity has been shown to have an exact cubic dependence (*9*). This is the same temperature dependence as that of the strongly magnetic metals. It is now interesting to note that very pure W (*10*) is T^5, the same as most nontransition metals, while very pure Nb is T^3. We

Table 2. The transition elements. Under each element the temperature is the superconducting transition temperature (*18*), if known; Mag. indicates that the material is strongly magnetic. The T numbers below give the temperature dependence of the electrical resistivity at low temperatures for the purest samples of each element found in the literature. A T^5 dependence is almost always observed in the nontransition elements. The lowest number under each element indicates the heat of atomization in kilocalories per gram atom at 298°K.

III	IV	V	VI	VII	VIII		
Sc	*Ti*	*V*	*Cr*	*Mn*	*Fe*	*Co*	*Ni*
	0.4°K	5.4°K	Mag.	Mag.	Mag.	Mag.	Mag.
	$T^{5.3}$	$T^{3.4}$	$T^{3.2}$	$T^{2.0}$	$T^{3.3}$	$T^{3.3}$	$T^{3.1}$
88	112.7	123	95	66.7	99.5	101.6	102.8
Y	*Zr*	*Nb*	*Mo*	*Tc*	*Ru*	*Rh*	*Pd*
	0.6°K	9.3°K	0.9°K	7.9°K	0.47°K		
T^5	$T^{4.5}$	$T^{3.0}$	T^5		$T^{4.7}$	$T^{4.6}$	$T^{3.2}$
98	146	173	157.5		155	133	91
Lu	*Hf*	*Ta*	*W*	*Re*	*Os*	*Ir*	*Pt*
	0.2°K	4.4°K	0.01°K	1.4°K	0.69°K	~0.1°K	
	$T^{4.7}$	$T^{3.8}$	$T^{5.0}$	$T^{4.6}$	$T^{4.7}$	$T^{4.7}$	$T^{3.7}$
95	160	186.8	200	187	187	155	135.2

conclude that there is not much *s-d* scattering in W and that *s-d* scattering is the major process leading to normal-state resistivity in Nb.

To summarize our previous arguments and extend them somewhat, we consider that while there is a large *s-d* interaction in V, Nb, and Ta, in Mo and W this interaction is small, owing to the intrinsic stability of a half-filled *d*-shell along with its involvement in strong lattice bonding. There is the correlation between generally high superconducting transition temperatures in the column headed V (Table 2) and a large *s-d* interaction; for W and near Mo there is a low T_c, together with low *s-d* interaction and a high lattice stability. Because of the maximum stability of the crystal lattice and electron configuration near column VI, we interpret the large *s-d* interactions in column V to be caused by the tendency of the valence electrons in these elements to assume the configuration of column VI. This leads us immediately to a picture for the occurrence of superconductivity in the transition metals.

Of all the rare earths along with Sc and Y only La becomes superconducting. La has a T^3 dependence of resistivity (*14*) at low temperatures as compared to Y, which has a T^5 dependence (*11*). This further substantiates the contention of Hamilton and Jensen that an incipient *f* level exists for La (*15*).

Superconductivity has not been observed in Pd or Pt. These elements are highly paramagnetic and close to ferromagnetic when doped with small amounts of magnetic elements (*16*). The resistivity behavior of Pd and Pt is nearly T^3, very much like the T^3 behavior observed in the magnetic elements from Cr to Ni.

Let us again consider Nb, since it has the highest T_c. In our picture, the *d* electrons are rather localized and also strongly involved in lattice bonding, while the *s* electrons are itinerant as usual. Although distinguishing between electrons this way is rather artificial, it is useful for the discussion. Our model is somewhat different from that of Zener (*17*), in which he describes some properties of transition elements. We think that bonding between adjacent Nb *d*-shells would be stronger if there were more *d* electrons, since they would be approaching the cohesion maximum that is between columns V and VI (Table 2). For the ground state configuration of Nb the *s* electron wave function, whatever it may be, will reflect the involvement of the *s* electrons in the *d* bonding. A measure of this involvement is the *s-d* scattering as deduced from resistivity data. The wave function of the free electrons is thus modified. We may view this process in a time-dependent scale as follows: Metastable *d* state configurations are constantly being formed by *s-d* scattering. It is possible that when two *s-d* scatterings occur on adjacent Nb atoms at nearly the same time, the pair of metastable states will live longer than a single state because of the enhanced cohesion between them. On a time average, this will be manifested as an attractive interaction between pairs of *s* electrons. Schematically this would be written $s \rightarrow d^5 = d^5 \leftarrow s$ where the double line indicates additional lattice bonding. This results in correlation and attractive interaction between *s* electrons as required for superconductivity.

Resistivity data indicate a large *s-d* scattering also in V and Ta. Thus the same process would apply to these elements as to Nb. In column VII (heading VII in Table 2), although the evidence is not as complete, an essentially similar process presumably will occur as in column V. A crystal structure change on going from column VI to VII further complicates this situation.

In our model we try to show that for the transition metals the interaction between *d*-shells is essential for providing a correlation between *s* electrons and hence superconductivity. At the extreme right of the transition elements, Pd and Pt have a ground state configuration somewhere between d^9s^1 and d^{10}. A tendency for the itinerant electrons to scatter into the *d*-shell and form a somewhat stable d^{10} configuration would account for the strong *s-d* scattering as deduced from the resistivity data. However, the result of this configuration will not be enhanced bonding nor will any attractive interaction between *s* electrons follow.

In conclusion we have been able for the first time to establish a connection between high-temperature superconductivity and bonding electrons—in particular, the half-filled *d*-shell. An insight into the instability of the high-temperature superconductors thus might emerge.

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Biotite Flakes: Alteration by Chemical and Biological Treatment

Abstract. *Biotite alteration under acid conditions proceeds differently from the generally accepted pathway of transformation to vermiculite in which hydrated cations cause interlayer expansion, resulting in a dark-colored peripheral band on mica particles. Acid solutions of synthetic or biologic origin remove octahedral ions, leaving a fragile matrix of amorphous material.*

Most discussions of primary mineral alteration and clay mineral formation in the biosphere are restricted to consideration of inorganic chemical reactions. Such reactions are of significance in explaining the continuum of processes that may take place between magmatic crystallization and ultimate degradation of lattice minerals.