

of our study represent a control for the socioeconomic variable. Cadmium toxicity is also receiving increased attention (10), although studies of its effect on behavioral disturbances are lacking.

The definition of LD used in the present study, although typical, is overly general, having been selected originally for reasons unrelated to hair element study. Consequently, statements as to what specific behaviors account for the reported relation between groups and metals cannot be made. Also, the possible importance of the time difference (2½ months) in collecting hair from LD group and from the control group is unknown. Nevertheless, the high levels of significance reported here, the presence of geographical and socioeconomic controls, the consistency with a growing literature on the subject, and the general failure of educative techniques with many LD children suggests that element patterns may prove not only a fruitful diagnostic procedure, but may also provide answers pertaining to etiology and treatment.

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## Entropy Estimates of Garnets and Other Silicates

As a way of estimating third law entropies of silicates, Saxena (1) has presented equations in which there is a linear relationship between the molar entropy at 298.15°K and the molar volume. He has used these equations to estimate the entropy of the garnets pyrope ( $Mg_3Al_2Si_3O_{12}$ ) and almandine ( $Fe_3Al_2Si_3O_{12}$ ). The equation applied to pyrope was obtained from the data for the orthosilicates of Be, Mg, Ca, and Zn, and the equation for almandine was based on the entropy of  $FeSiO_3$  and  $MnSiO_3$ . The procedures used by Saxena are open to criticism on two counts: (i) the linear relationship between entropy and volume completely ignores the well-known role of mass, and (ii) for compounds containing transition metal ions, significant magnetic contributions to entropy are neglected.

In essence, Saxena (1) provides expressions for estimating the entropy of lattice vibrations. It has long been known (2) that "lattice" entropy can be estimated satisfactorily in terms of atomic mass. Of course, volume will also be a factor. Indeed, Cantor (3) has shown, from the Debye theory of specific heats, that lattice entropy  $S$  is related both to molar mass  $M$  and to molar volume  $V$  by the equation

$$S = A + \frac{3}{2} nR \ln MV^{2/3} \quad (1)$$

where  $A$  is nearly constant for closely related compounds,  $n$  is the number of gram-atoms in a mole of the crystal, and  $R$  is the gas constant. Values of  $A$  for the orthosilicate series of the formula  $M_2^{II}SiO_4$  are given in Table 1. These values were obtained from the experimental

Table 1. Values of  $A$  for orthosilicates of the formula  $M_2^{II}SiO_4$ .

Silicate	Formula	$A$ (gibbs/mole)
Phenacite	$Be_2SiO_4$	-133.01
Forsterite	$Mg_2SiO_4$	-133.02
Ca-olivine	$\gamma-Ca_2SiO_4$	-135.36
Willemite	$Zn_2SiO_4$	-136.47
Average		-134.47

Table 2. Calculation of the entropies of tephroite and fayalite.

Formula	Lattice entropy (Eq. 1)	Magnetic entropy (Eq. 3)	Estimated entropy	Experimental entropy (4)
$Mn_2SiO_4$	30.30	7.12	37.42	$39.0 \pm 1.0$
$Fe_2SiO_4$	29.83	6.40	36.23	$35.45 \pm 0.4$

entropies, at 298.15°K, critically compiled by Robie and Waldbaum (4). At 298.15°K, Ca-olivine is more stable than larnite ( $\beta-Ca_2SiO_4$ ), and it is Ca-olivine that is correlated by Eq. 1. Saxena (1) specifically excludes Ca-olivine from his correlation for orthosilicates, presumably because his estimated entropy was too high by 9.15 gibbs/mole.

A more directly applicable form of Eq. 1 is the expression

$$S_y = S_x + \frac{3}{2} nR \ln [M_y V_y^{2/3} / (M_x V_x^{2/3})] \quad (2)$$

where  $y$  refers to a compound whose entropy is to be estimated and  $x$  signifies a reference compound, that is, one chemically and structurally similar to  $y$  whose entropy is known. For instance, to estimate the entropy at 298.15°K of pyrope ( $Mg_3Al_2Si_3O_{12}$ ), we use grossularite ( $Ca_3Al_2Si_3O_{12}$ ) as the reference compound. Substituting in Eq. 2 the experimental data tabulated in (1), we have pyrope entropy =  $1.5(20)1.987 \ln [403.15(113.27)^{2/3} / (450.454(125.3)^{2/3})] = 57.7 = 47.07$  gibbs/mole.

The estimation of entropy at 298.15°K for crystalline silicates containing transition metal ions requires an additional term to account for the disorder of magnetic moments. For compounds of the first transition series, Ulbrich and Waldbaum (5) have shown that magnetic entropy  $S_m$  can be approximated from the spin quantum number  $S$  by the equation

$$S_m = R \ln (2S + 1) \quad (3)$$

For example, in rhodonite ( $MnSiO_3$ ),  $S$  for divalent manganese is 5/2 and, from Eq. 3,  $S_m = 3.561$  gibbs/g-atom. The lattice entropy at 298.15°K, estimated from enstatite ( $MgSiO_3$ ) according to Eq. 2, is 21.26 gibbs/mole. The sum,  $3.561 + 21.26 = 24.82$  gibbs/mole, agrees quite closely with the experimental entropy of  $24.5 \pm 0.5$  gibbs/mole given in (4). We can estimate (Table 2) the entropies of the orthosilicates tephroite ( $Mn_2SiO_4$ ) and fayalite ( $Fe_2SiO_4$ ) from Eq. 3 by calculating lattice entropy from Eq. 1, using the average  $A$  (-134.47 gibbs/mole) ob-

tained from the four diamagnetic orthosilicates listed in Table 1.

A similar procedure can be used to estimate the entropy of the garnet almandine. Using grossularite as the reference compound in Eq. 2, we obtain an estimated lattice entropy for almandine of 60.34 gibbs/mole. Since  $S = 2$  for  $\text{Fe}^{2+}$ , the magnetic entropy (from Eq. 3) is 9.59 gibbs per mole (that is, 3 g-atoms). Thus, the estimated entropy at 298.15°K is 60.34 + 9.59 = 69.93 gibbs/mole, a value somewhat greater than the 68.13 gibbs/mole estimated by Saxena (1).

It is instructive to compare Saxena's correlation with the methods given here for estimating the entropy of another garnet. For andradite ( $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$ ), the entropy at 298.15°K ( $78.7 \pm 1.3$  gibbs/mole) has been computed (6) from heat capacity data (7). The molar volume, 131.65  $\text{cm}^3$ , is obtained from the unit cell parameter, 12.048 Å, given in Wyckoff (8). The substitution of 131.65  $\text{cm}^3$  in equation 2 of Saxena (1) yields an entropy of 94.32 gibbs/mole. Since  $S = 5/2$  for  $\text{Fe}^{3+}$ ,  $S_m = 2R \ln 6 = 7.12$  gibbs/mole. If grossularite is used as the reference compound in Eq. 2, we obtain 66.85 gibbs/mole as the lattice entropy of andradite; this added to the magnetic entropy gives an entropy of 73.97 gibbs/mole, an estimate much closer to the experimental value than is predicted from (1). This example amply illustrates the pitfall of estimating entropy from volume alone.

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My report (1) was written primarily in an effort to develop an empirical relationship between the molar volume and entropy  $S$  of silicates that would yield somewhat better estimates of third law entropies than those obtained by the summation of the entropies of the constituent oxides. It still serves that pur-

Table 1. Comparison of the entropy estimates of silicates by three different methods. Averages of the constant  $A$  used [equation 1 of (2)] are -134.47, -87.67, and -283.33 gibbs/mole for ortho-, meta-, and framework silicates, respectively. Abbreviations: exp, experimental; calc, calculated; oxides, oxide summation; N.P., not possible without more data.

Silicate	$S_{\text{exp}} - S_{\text{calc}}$		$S_{\text{exp}} - S_{\text{oxides}}$
	Saxena	Cantor	
<i>Orthosilicates</i>			
$\text{Be}_2\text{SiO}_4$	0.14	1.46	-1.25
$\beta\text{-Ca}_2\text{SiO}_4$	0.33	2.75	1.62
$\gamma\text{-Ca}_2\text{SiO}_4$	-9.15	-0.84	-0.08
$\text{Mg}_2\text{SiO}_4$	0.67	1.50	-0.01
$\text{Zn}_2\text{SiO}_4$	0.38	-1.94	0.66
$\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	-2.25	N.P.	-12.63
$\frac{1}{2}(\text{Ca}_3\text{MgSi}_2\text{O}_8)$	-1.53	+3.24	-4.54
<i>Metasilicates</i>			
$\text{CaSiO}_3$	-0.97	-0.83	0.22
$\text{CaSiO}_3$ (pseudo)	0.25	0.44	1.08
$\text{CaAlSiO}_6$	2.36	0.18	3.04
$\text{CaMgSi}_2\text{O}_6$	0.54	-0.80	-1.50
$\text{MgSiO}_3$	0.25	0.33	-0.10
$\text{NaAlSi}_2\text{O}_6$	1.35	0.72	-2.94
<i>Feldspars and feldspathoids</i>			
$\text{KAlSi}_3\text{O}_8$ (microcline)	0.03	-3.27	5.49
$\text{KAlSi}_3\text{O}_8$ (sanidine)	0.11	-3.37	5.52
$\text{NaAlSi}_3\text{O}_8$ (low albite)	1.30	-1.11	5.48
$\text{NaAlSi}_3\text{O}_8$ (high albite)	1.15	-1.20	5.48

pose for silicates of nontransition elements. The entropy-volume relation (1) was found to be particularly good for silicates with spherical ions, a point that I emphasized. I did not consider the transition elements because of a lack of data, although I did discuss the entropy of almandine on the basis of the data on  $\text{Fe}_2\text{SiO}_4$  and  $\text{Mn}_2\text{SiO}_4$ .

It is well known that for spherical ions there is a distinct correlation between mass and volume. The significant correlation found between the entropy and volume of the silicates indirectly attests to this fact. It was my hope that Cantor's (2) equations would provide significant improvement in the entropy estimates. Unfortunately, Table 1 shows that this is not true. Cantor's (2) calculated entropies of almandine and pyrope (69.93 and 47.07 gibbs/mole, respectively) also do not differ significantly from mine (68.13 and 47.47, respectively). As I discussed in (1), equation 2 was based on

Table 2. Comparison of the entropy estimates of silicates of transition metal ions.

Silicate	$S_{\text{exp}} - S_{\text{calc}}$ (Cantor)	$S_{\text{exp}} - S_{\text{oxides}}$
$\text{Fe}_2\text{SiO}_4$	-0.78	-1.95
$\text{Mn}_2\text{SiO}_4$	1.58	0.58
$\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$	4.73	-0.06

only two entropy values and therefore should not generally be used without additional data. Table 2 shows that for silicates of transition metals the entropy estimates of Cantor (2) are no better than those obtained by the oxide summation method.

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## Checkerboards and Color Aftereffects

The cover of the 9 April 1976 issue of *Science* (1) purports to show that the human visual system analyzes patterns into Fourier components rather than into local features. As such, the demonstration is quite misleading since it can be understood on rather more simple grounds. There has, indeed, been rather substantial experimental evidence to suggest that the eye may behave in this

way, although the matter is still controversial. At issue is not whether a Fourier representation of visual space can be useful in studying visual phenomena (the answer is a clear yes), but whether signals moving in the optic nerve from retina to cortex are coded in terms of a Fourier analysis of a scene rather than in some more straightforward representation.