the positive reaction to the synthesized product.

It is difficult to define an exact mechanism for the responses to MSG. Since L-glutamic acid is present in large amounts in the central nervous system and has been suggested as a neurohumoral transmitter (12), it seemed reasonable to assume a central nervous mechanism for all the sensory phenomena. However, the results of the local perfusion of one extremity isolated from the rest of the body has dispelled this theory as accounting for all the symptoms. There is usually no sensation immediately after intravenous administration of the substance. However, after 17 seconds there is an intense burning, first in the chest, then spreading centripetally to involve the shoulders, neck, forearms, and abdomen.

In two of the six individuals given 500 mg intravenously, the burning sensation traveled down the midline of the abdomen, bifurcated and continued into the thighs. This response, combined with the isolated limb perfusion, implicates arterial receptor. The chest pressure after intravenous injection seemed somewhat like anginal pain. This pain is also similar to that produced on stimulation of the aortic chemoreceptors (13). The lack of change in electrocardiogram would be consistent with either.

Headache occurred consistently in two of our 56 subjects; it was the primary complaint of two correspondents in the original description of the disease; and we have received four letters from individuals in whom headache was the only symptom. The headache pattern is that of a combined vascularmuscular contraction headache. The significance of L-glutamic acid in the epidemiology of this common headache is still undetermined.

A review of experiments on oral and intravenous administration of MSG has revealed none of the reactions reported here. Because in the two conditions for which MSG has been prescribed (hepatic coma and mental retardation) the subjective response of the individual is unreliable if elicitable at all, it is not surprising that the symptoms have not been reported.

Since glutamic acid is present in large amounts both in the body and in some foods, the Food and Drug Administration places MSG in the category termed "generally regarded as safe.' No limitation is placed on its use as a food additive (1). We now have shown that MSG can produce undesirable effects in the amounts used in the preparation of widely consumed foods.

HERBERT H. SCHAUMBURG Saul R. Korey Department of Neurology, Albert Einstein College of Medicine, Bronx, New York 10461

ROBERT BYCK

Departments of Pharmacology and Rehabilitation Medicine

ROBERT GERSTL

Department of Pharmacology JAN H. MASHMAN

Saul R. Korey Department of Neurology

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Discovery of the Garnet, Khoharite?

Thirty years ago, Sir Lewis [Fermor] (1) introduced the name khoharite in order to account for the composition of a garnet from the Jagersfontein diamond mine in South Africa. The name was assigned to the end-member composition Mg₃Fe₂³⁺(SiO₄)₃, but the garnet example that was analyzed contained merely 10.63 percent of this "molecule."

Quite recently Mason et al. (2) reported a garnet of most unusual composition, found in the Coorara chondritic meteorite. On the basis of an analysis by electron microprobe, they report the composition to be as follows: MgO, 36.9 to 39.5 percent; SiO₂, 37.1

to 39.6 percent; and FeO, 23.5 to 25.0 percent. Inasmuch as this method, as ordinarily carried out, is incapable of indicating the oxidation state of the iron, the question immediately arises: Does the analysis conform to that of a garnet if the iron is assumed to be trivalent instead of divalent? They admitted "it is difficult to reconcile this composition $[(Mg_{.75}Fe_{.25})_2SiO_4]$ with that of a garnet." The crystal chemistry of garnets is sufficiently well known to permit a stronger statement: It is impossible to reconcile this composition with that of a garnet.

The general formula for an anhydrous garnet can be written $A_3B_2(XO_4)_3$, where A is normally a divalent cation, B is normally trivalent, and X is normally Si, but can be other cations with a coordination number four (CN = 4). The CN of B is six and that of A is eight, and the total number of cations is eight. The fundamental structure for garnet depends on the symmetrical arrangement of the 96 oxygen atoms according to the requirements of the space group Ia3d. (Here the discussion will be concerned with a smaller unit: one-eighth of the contents of the unit cell.)

If the composition shown by Mason et al. (2) is expressed in elemental form and the cations are summed to eight, this result is obtained:

A = 3 Mg(6 plus charges) $B = 1.1 \text{ Fe}^{3+} + 0.9 \text{ Mg}$ (5.1 plus charges) $X = 2.7 \text{ Si} + 0.3 \text{ Fe}^{3+}$ (11.7 plus charges) It is immediately noticeable that the sum of cationic charges is merely 22.8, whereas that required to balance the 12 oxygens is 24. Even assuming all iron as ferric, this discrepancy exists.

A most precise measurement given by Mason et al. (2) is that of the unitcell dimension $(a = 11.51_5 \text{ Å})$, and again, this value is smaller than that of any known garnet that does not contain aluminum. The calculated d for khoharite is 11.637 Å (3), but the above composition contains substitutions of atoms with larger radii in each instance. That is, the radius $Fe^{3+} > Si$ and Mg >Fe³⁺, whereas Fe²⁺ \geq Fe³⁺.

A somewhat speculative conclusion arises from these two different crystalchemical considerations: Not only must most, if not all, of the iron be trivalent, but the analysis of Mason et al. (2) fails to report some cation with small radius and high valence. Two possibilities suggest themselves-phosphorus and sulfur $(P_2O_5 \text{ and } SO_3)$, both of which could substitute for Si. A garnetoid containing 38.5 percent of P_2O_5 is griphite (4).

However, assuming for khoharite a =11.637 Å, it is possible to calculate (5)the amounts of P and S atoms that would have to be substituted for Si in order to obtain the measured value 11.51_5 Å, and these amounts are by no means insignificant. Although it is difficult to believe that Mason et al. (2) could have missed a major constituent on analysis with the electron microprobe, there is something enigmatic about the failure of the composition to conform to the theoretical requirements for a garnet structure. The question remains: Did Mason et al. (2) discover a complex isomorphic varient of khoharite? If so, what is its composition?

DUNCAN MCCONNELL Department of Mineralogy, Ohio State University, Columbus 43210

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17 July 1968

Alternative Explanation of the Garnet Occurrence in a Meteorite

Recently, Mason, Nelen, and White reported (1) the occurrence of a garnet in the Coorara meteorite. They found this garnet to have a lattice constant of 11.515 Å and suggested that it may have the probable composition, $Mg_3Fe_2Si_3O_{12}$. I believe that this composition is very unlikely for a garnet with the given lattice constant and that if this garnet contains only Mg^{2+} , Fe³⁺, Fe²⁺, and Si⁴⁺ cations, it must have a substantial amount of octahedrally coordinated Si⁴⁺ ion in it with an approximate formula

$\{<Mg,Fe^{2+}>_{3}\}$

 $[Fe^{3+}_{0,4} < Mg, Fe^{2+} >_{0,8}Si_{0,8}](Si_3)O_{12}$

where the outer braces have the meaning given by Geller [Table 1 in (2)], and the pointed brackets indicate a mixture of different ions (in this case, Mg^{2+} and Fe^{2+}) and of presently unknown amounts.

In addition to the lattice constant, Mason et al. give the results of an

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electron microprobe analysis, but the composition thereby obtained is not in agreement with the garnet formula they suggest. They offer the explanation that the microprobe beam may not have sufficient resolving power to give a correct analysis in this case; otherwise, they "must consider the possibility of a nonstoichiometric composition, maybe a 'stuffed' garnet with a total of six 6- and 8-coordinated cations for 12 oxygen ions instead of five as in the normal garnet structure." Apparently, the formula for the suggested "stuffed" garnet would be

$\{Mg_3\} [Mg_{1.5}Fe_{1.5}] (Si_3)O_{12}$

(For electrostatic charge balance the ion would be divalent.) It should suffice to say that the garnet structure cannot contain this excess of cations: there is simply no space for them in the unit cell, nor would the space group allow their presence. Nevertheless, I must accept the suggestion that the composition obtained by the microprobe analysis is probably not correct.

I am quite confident that the lattice constant for the garnet is far too small to be that of $Mg_3Fe_2Si_3O_{12}$. Unfortunately, although the synthesis of a garnet with this formula has been reported (3), its lattice constant was not reported, but it is not too difficult to predict what it should be. I do this in the following way: Table 1 shows that there is an almost constant difference of 0.20 Å between the lattice constant of an

 $\{A_3\} [Fe_2] (B_3)O_{12}$

and

${A_3} [A_{1_2}] (B_3)O_{1_2}$

garnet. The lattice constant of Mg₃Al₂- Si_3O_{12} is 11.46 Å; therefore, the predicted value of Mg₃Fe₂Si₃O₁₂ is 11.66 Å. [I should point out that the lattice constant of $Mn_3Fe_2Si_3O_{12}$ had been successfully predicted (4) in this way.] This is 0.14 Å larger than that reported for the Coorara meteorite garnet.

Recently, Ringwood showed (5) that a garnet with homogeneous composition equivalent to the formula

{Mg₃} [Al_{0.8}Mg_{0.6}Si_{0.6}] (Si₃)O₁₂

prepared at 250 kb and 900°C has the lattice constant 11.477 Å. He also showed that this garnet begins to form at a pressure of about 90 kb, and its formation is virtually complete by 110 kb (all at 900°C). In this case, some of the Si⁴⁺ ion has 6-coordination; in

Table 1. Lattice constants (2) of [Fe³⁺] and [Al³⁺] garnets.

Garnet	(Å)	Δ <i>a</i> (Å)
$\begin{array}{c} Ca_3Fe_2Si_3O_{12}\\ Ca_3Al_2Si_3O_{12} \end{array}$	12.059 11.851	0.208
$\begin{array}{l} Mn_{3}Fe_{2}Si_{3}O_{12}\\ Mn_{3}Al_{2}Si_{3}O_{12} \end{array}$	11.82 11.621	.20
$\begin{array}{c} Ca_{3}Fe_{2}Ge_{3}O_{12}\\ Ca_{3}Al_{2}Ge_{3}O_{12} \end{array}$	12.320 12.120	.200
$\begin{array}{l} Mn_3Fe_2Ge_3O_{12}\\ Mn_3Al_2Ge_3O_{12} \end{array}$	12.087 11.902	.185
$\begin{array}{c} Cd_{3}Fe_{2}Ge_{3}O_{12}\\ Cd_{3}Al_{2}Ge_{3}O_{13} \end{array}$	12.261 12.077	.184
	Average	.20

stishovite (6), a high-pressure modification of SiO₂, all the silicon has 6coordination. The replacement of one Al³⁺ by one Fe³⁺ ion per formula unit causes an increase of 0.10 Å in the lattice constant; thus a garnet

$\{Mg_3\}$ [Fe_{0.8}Mg_{0.6}Si_{0.6}] (Si₃)O₁₂

would have the lattice constant 11.56 Å, which is only about 0.04 Å larger than that reported for the garnet found in the Coorara meteorite. Replacement of Mg²⁺ by small amounts of Fe²⁺ in either the octahedral or dodecahedral sites would not increase the lattice constant substantially, so that the garnet could contain more Fe and less Mg. A further decrease of Fe^{3+} ion and increase of $[Mg^{2+}, Si^{4+}]$ in octahedral sites would decrease the lattice constant further. In fact, on the basis of the arguments given, a more likely formula would be that given at the beginning of this communication.

Mason et al. (1) have already indirectly indicated the low probability for an olivine-garnet transformation. Ringwood (7) has not only demonstrated the olivine to spinel transformation, but also the likelihood of pyroxene to garnet transformation (5). Is it not possible that the garnet in the meteorite replaced pyroxene + olivine instead of olivine alone? An example of a possible reaction for such an occurrence is

7 Mg_{1.5}Fe_{0.5}SiO₄ + 5 MgSiO₃ $\xrightarrow{+0}$ $2{Mg_3}$ [FeMg_{0.5}Si_{0.5}] (Si₃)O₁₂ + 5 Mg_{1.7}Fe_{0.3}SiO₄

This is just an example; compositions of the reactants may be easily varied to fit the analyses if they could be accurately made. We must still have a source of a small amount of oxygen for the $Fe^{2+} \rightarrow Fe^{3+}$ conversion, but this scheme requires even less such oxygen than that suggested by Mason et al. (1).