

# Chromian–manganooan augite in the interchondrule matrix of the Tieschitz (H3) chondritic meteorite

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## Abstract

The Tieschitz chondrite is a disequilibrium assemblage of silicate, metal and sulphide occurring together or separately as chondrules and clasts that generally have opaque rims (matrix) of fine-grained material. Translucent, silicate-rich matrix fills channels that occur sporadically between chondrules and clasts. An angular fragment of twinned 'clinoenstatite' was found to be rimmed with chromium- and manganese-rich augite and surrounded by opaque matrix. The whole is set within the largest area of translucent (white) interchondrule matrix encountered. It is suggested that reaction between crystallizing undersaturated translucent matrix, opaque matrix, and clinoenstatite probably led to the partial replacement of clinoenstatite by chromian–manganooan augite at high temperature.

KEYWORDS: chondrites, meteorites, Tieschitz, augite.

## Introduction

THE Tieschitz chondrite is a disequilibrium mineral assemblage of silicate and metal–sulphide chondrules and clasts, almost all of which are rimmed by fine-grained opaque matrix material. Outside the rims, channels that occur sporadically between the chondrules are filled with translucent, 'white' matrix (Christophe-Michel-Levy, 1976; Hutchison *et al.*, 1979). White matrix is rich in normative nepheline and albite, both of which have been identified as crystal fragments within it. Other materials that may be present within white matrix are olivine, low-Ca pyroxene, augite, sulphide, metal and opaque matrix. Apart from the last, these probably originated as fragments of chondrules. Hutchison *et al.* (1979) presented evidence that two deformed chondrule-like objects were plastic at the time of accretion, and Bevan and Axon (1980) remarked on some metal–sulphide chondrules that aggregated when in a semi-molten state. Hutchison *et al.* (1979) also noted that white matrix has a bulk composition similar to that of some chondrule mesostases, and argued that it probably represents fractionated chondrule liquids expressed from deformed chondrules.

On the basis of these observations, Hutchison *et al.* (1979) and Bevan and Axon (1980) suggested that the Tieschitz assemblage had accreted at  $(800 \pm 100)^\circ\text{C}$ . This hot accretion hypothesis has received little support; rather, it was attacked

recently by Morgan *et al.* (1985), who interpreted the abundances of various trace elements, especially volatiles, in H-group chondrites as the result of cold accretion followed by a period of thermal metamorphism, a suggested origin that has been popular for over twenty years (see e.g. in Dodd, 1981). However, the hot accretion hypothesis predicts that reactive materials in physical contact, for example low-Ca pyroxene and nepheline, should show some signs of reaction, in this case to form olivine plus albite. Because no post-accretion reaction appeared to have occurred (Wlotzka, 1983), Hutchison *et al.* (1979) suggested that hot accretion occurred during a period of rapid cooling. Rapid cooling immediately following accretion was also supported by the observations of Bevan and Axon (1980). Evidence of reaction between the various components of the meteorite has since been sought more carefully; the following observations are the result.

## Reaction in Tieschitz interchondrule matrix

A search of our polished thin-section (area  $4\text{ cm}^2$ ) under the petrological microscope in transmitted light yielded no evidence of direct reaction between nepheline-normative, undersaturated white matrix and low-Ca pyroxene. However, within the largest interchondrule area of white matrix in the section lies an irregularly shaped fragment of optically twinned low-Ca pyroxene that appears to be

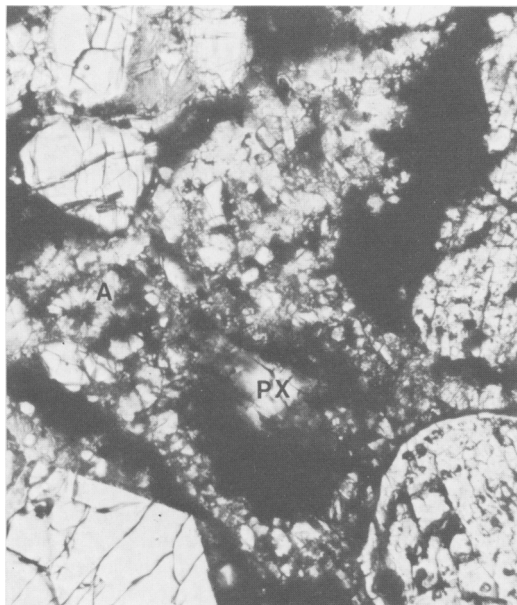


FIG. 1. Micrograph, transmitted plane-polarized light, field 300  $\mu\text{m}$  wide. Tieschitz, largest area of 'white' matrix encountered in 4  $\text{cm}^2$  thin-section. PX = twinned clinoenstatite fragment, with dark corona of irregular thickness set in transparent, clastic, 'white' matrix that is delineated by the opaque rims of surrounding chondrules and clasts. At A, fragment of 'white' matrix has radial structure suggestive of spherulitic crystallization.

surrounded by a translucent grey, to opaque black, corona (Fig. 1). The interchondrular area has the rough outline of an isosceles triangle with two sides of 350  $\mu\text{m}$ , the third being 300  $\mu\text{m}$ . Along one of the longer sides, some patches of white matrix have a radiating structure suggestive of spheroidal crystallization (A in Fig. 1). Although the white matrix in general appears to have suffered post-accretion, mild cataclasis, the above observation indicates that areas up to 50  $\mu\text{m}$  across may have remained coherent.

Under reflected light the angular low-Ca pyroxene fragment was seen largely to be surrounded by opaque matrix, which gives the appearance of the dark corona in transmitted light. Opaque, interchondrular matrix is a fine-grained clastic mixture essentially composed of olivine, pyroxene, sulphide and a sodic plagioclase component. Metal may also be present (Ashworth, 1981; Nagahara, 1984; Alexander *et al.*, 1984). The grain-size lies in the micrometre to sub-micrometre range. Around the edge of the low-Ca pyroxene fragment and along cleavage cracks penetrating from the exterior lies material with mean atomic number intermediate

between those of the pyroxene and opaque matrix (Fig. 2a). This material proved to have the composition of augite; its distribution is clearly revealed by the high Ca concentration (Fig. 2). However, enrichment in Mn (Fig. 2) and Cr accompanies Ca in the augite. A high Fe content (Fig. 2) reflects the distribution of the opaque matrix, and the width of the augite overgrowth, from 2–15  $\mu\text{m}$ , appears to correlate with the width of opaque matrix adjacent to it. However, this correlation is only approximate and it should be stressed that in the third dimension, the geometry of the associated materials is unknown. A further complication is that the lower area of opaque matrix appears to have been displaced by some 10  $\mu\text{m}$  to the left relative to that adhering to the augite overgrowth and low-Ca pyroxene core (Fig. 2a).

### Chemistry

The chemical compositions of the core and rim of the low-Ca pyroxene fragment and of two parts of the chromian-manganian augite are presented in

TABLE 1. Manganian augite and associated materials

	1	2	3	4	5	6
SiO <sub>2</sub>	58.5	55.4	50.7	53.3	33.0	31.3
TiO <sub>2</sub>	0.03	0.04	0.56	0.32	0.23	0.12
Al <sub>2</sub> O <sub>3</sub>	0.20	0.49	3.20	2.45	3.25	2.42
Cr <sub>2</sub> O <sub>3</sub>	0.58	0.93	2.68	2.40	0.21	0.33
FeO	3.52	4.85	5.75	4.54	29.5	35.9
MnO	0.28	0.64	2.64	2.57	0.38	0.44
MgO	36.8	33.7	17.2	22.0	17.6	18.9
CaO	0.22	0.91	15.8	12.7	1.81	0.30
Na <sub>2</sub> O	<0.05	0.09	0.47	0.49	1.38	1.71
K <sub>2</sub> O	—	—	—	—	0.11	—
S	—	—	—	—	0.1	0.1
Sum	100.1	97.1	99.0	100.8	87.6	91.5
Pyroxene cations to six oxygens						
Si	1.994	1.966	1.887	1.910		
Al(IV)	0.006	0.021	0.113	0.090		
Al(VI)	0.002	0.000	0.028	0.013		
Ti	0.000	0.002	0.016	0.009		
Cr	0.014	0.026	0.078	0.069		
Cr	0.100	0.145	0.179	0.135		
Mn	0.008	0.019	0.083	0.077		
Mg	1.867	1.781	0.954	1.174		
Ca	0.008	0.034	0.630	0.488		
Na	0.000	0.006	0.033	0.034		
Sum	1.997	2.013	2.001	1.999		

1. Optically twinned pyroxene core, mean of two analyses  $\text{Wo}_{0.5}\text{En}_{94}$ .
2. Edge of core, point 2, Fig. 2a  $\text{Wo}_{1.7}\text{En}_{90}$ .
3. Manganian augite rim, point 3, Fig. 2a.  $\text{Wo}_{34}\text{En}_{52}^{\text{Mn}}\text{Fs}^{\text{Mn}}_{14}$ .
4. Manganian augite, point 4, Fig. 2a.  $\text{Wo}_{26}\text{En}_{63}^{\text{Mn}}\text{Fs}^{\text{Mn}}_{11}$ .
5. Opaque matrix, point 5, Fig. 2a, 5  $\mu\text{m}$  spot.
6. Opaque matrix, point 6, Fig. 2a, 5  $\mu\text{m}$  spot.

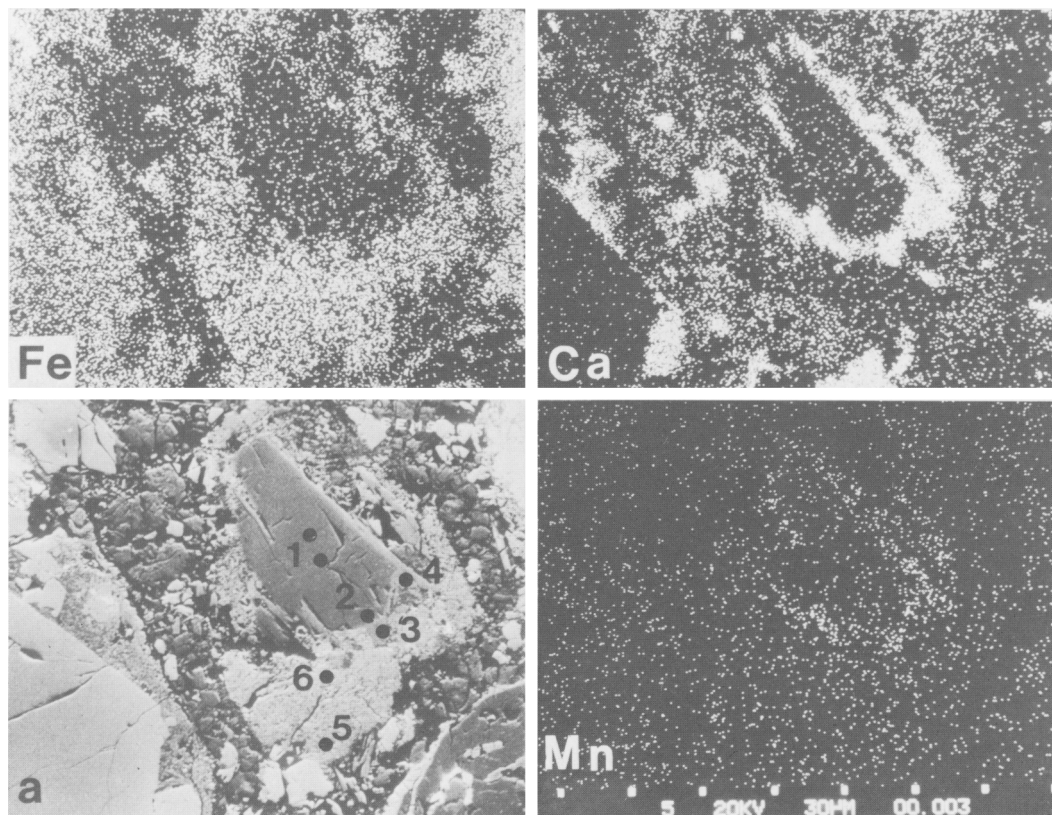


FIG. 2. (a) Back-scattered electron image of clinoenstatite fragment (1,2) with irregular rim of manganian augite (3,4), surrounded by opaque matrix (5,6), part of which has been displaced to the left (point 6 relative to point 3). The field has been rotated slightly anticlockwise relative to the elemental distribution maps. The high Fe content of olivine, pyroxene and sulphide accounts for a high mean atomic number, rendering opaque matrix bright on the back-scattered electron image. Fe distribution map shows Fe-rich opaque matrix thinnest to upper right of pyroxene, and set in Fe-poor 'white' matrix. Concentrations of Fe in 'white' matrix generally are Fe-olivines. Ca distribution shows a high concentration in manganian augite surrounding the Ca-poor clinoenstatite fragment, in Mn-poor augites in 'white' matrix, and in chondrule mesostasis in left of field. Note very low concentration in opaque matrix (e.g. 6) adjacent to manganian augite. Mn concentration correlates with Ca in augite overgrowth on clinoenstatite. Scale, 30  $\mu\text{m}$  between white markers.

Table 1. The core of the low-Ca pyroxene lies in the enstatite range; the polysynthetic twinning indicates that it is clinoenstatite. Its very low CaO content is typical of low-Ca pyroxenes in the meteorite in general, but especially of those within chondrules (Hutchison *et al.*, 1980), and the  $\text{Cr}_2\text{O}_3$  and MnO contents are unremarkable. Apparent enrichment of the rim in  $\text{Cr}_2\text{O}_3$ , FeO, MnO and CaO may partially have been caused by fluorescence produced by excitation of the manganian augite nearby. Because of its narrowness the chromian-manganian augite proved difficult to analyse. However, the figures obtained for  $\text{Cr}_2\text{O}_3$  and MnO are consistently higher than in the

adjacent opaque matrix or low-Ca pyroxene and must be real. The overgrowth has a variable composition of a stoichiometric chromian augite, approximately  $\text{Wo}_{30}\text{En}_{58}\text{Fs}'_{12}$ , when the MnO is attributed with FeO to the ferrosilite end-member.

The opaque matrix in contact with the manganian augite has, except for its low CaO content (0.3 wt.%), a chemical composition within the range established previously (e.g. Christophe-Michel-Levy, 1976; Huss *et al.*, 1981; Hutchison and Bevan, 1983; Wlotzka, 1983). The Ca distribution map (Fig. 2) indicates that this element increases in abundance away from the contact of opaque matrix with the augite. This was confirmed

quantitatively in a series of microprobe analyses using a slightly defocused beam (5  $\mu\text{m}$  diameter) at 10  $\mu\text{m}$  spatial intervals. More than about 30  $\mu\text{m}$  from the contact with manganoan augite the opaque matrix has a uniform and normal CaO content of about 1.8 wt.% (Table 1, cf. nos. 5 and 6). Thus the presence of manganoan augite on clinostatite is associated with depletion of opaque matrix in CaO in a zone some 30  $\mu\text{m}$  wide. Surprisingly, no corresponding systematic depletion in  $\text{Cr}_2\text{O}_3$  or MnO was observed.

### Interpretation

The association of chromian-manganoan augite with very low-Ca clinostatite has not previously been observed and, at the very least, must be extremely rare. In contrast, overgrowths of augite with low Cr and Mn contents on phenocrysts of very low-Ca pyroxene are not uncommon in chondrules (Ashworth, 1981; Hutchison *et al.*, 1980), so in this case crystallization of both phases from a single, fractionating chondrule liquid is most unlikely to have been responsible for their origin. This is supported by the observation that chromian-manganoan augite has developed along cleavage cracks within the clinostatite, indicating that the augite grew by replacement of its host. The augite is enriched in MnO by almost an order of magnitude over the host clinostatite; such enrichment in MnO has not yet been observed in chondrules (Rubin, 1984) and there is no experimental evidence to suggest that extreme enrichment in MnO could be produced in liquid by fractional crystallization of enstatite. Furthermore, the contact of the augite with the clinostatite is sharp, which indicates that an abrupt change in chemistry took place.

It is suggested that the clinostatite was precipitated as protoenstatite within a chondrule, which subsequently became disrupted, releasing the protoenstatite which inverted to the twinned monoclinic form (see e.g. Biggar, 1985). The fragment of clinostatite then became engulfed in opaque, fine-grained matrix material. There is no evidence to indicate the temperature at which this union took place, but subsequently both matrix and crystal must have been hot enough to sustain reaction between them. Mass balance exists between the Ca enrichment of the augite rim and Ca depletion in the 30  $\mu\text{m}$  wide zone of opaque matrix adjacent to it, this being powerful evidence of a genetic relationship between the augite and opaque matrix. However, there is no evidence of a systematic depletion of the adhering opaque matrix in Mn or Cr, both of which are enriched in the augite, so perhaps they diffused into the augite from a wider reservoir than the Ca, or perhaps their host

phases disappeared completely, leading to a general redistribution of Cr and Mn. Alternatively, if the clinostatite originally had been much larger, during partial dissolution to become its present size Cr and Mn may have been retained in the margin of the shrinking core. Concentration of these elements into a quarter of the original volume could have yielded the observed Cr content of the augite, but only half the Mn; Ca would need to have been supplied by another source. This possibility is less likely because it is more complex than the alternative of deriving all three elements from opaque matrix. Furthermore, the pyroxene is now enclosed in matrix and partial dissolution must have taken place elsewhere, there being no evidence that the opaque matrix was once liquid. If there were a genetic relationship between the augite rim and the neighbouring opaque matrix, three questions arise:

1. What was the source of the MnO?
2. At what temperature did the augite form?
3. What was the source of heat?

### The source of the MnO

Rubin (1984) described an unusual chondrule rim in the Allende, CV3, meteorite, that contains Cr- and Mn-rich orthopyroxene and Mn-rich olivine. Opaque matrix adjacent to this rim is undepleted in Cr and Mn and Rubin suggested that the rim had become enriched in these elements by the condensation of Cr and Mn volatilized from chondrules. The present case is different. Formation of the augite rim appears to have been sustained by the migration of Ca from adjacent opaque matrix, so unless the enrichment in manganese resulted from a different process (one alternative, deemed unlikely, was discussed above), opaque matrix must also have been the source of Mn and Cr. A glance at analyses nos. 5 and 6, Table 1, indicates, however, that opaque matrix in Tieschitz has about 0.4 wt.% MnO and 30 wt.% FeO. How then can the MnO/FeO ratio of the augite be about forty times that in the opaque matrix if this had been the source of its constituents? There are at least two possibilities: either CaO, MnO and  $\text{Cr}_2\text{O}_3$  originally occurred together in opaque matrix in an unstable phase that could readily release them, or the MnO/FeO ratio of opaque matrix was much higher when the augite formed than it is now. The most likely phase that might have been able to release significant CaO and MnO (also MgO) at low temperature is dolomite. In the unusual carbonaceous chondrite Yamato 82042, dolomite with up to 4 wt.% MnO is not uncommon (Grady *et al.*, 1986). Thus it is possible that the opaque matrix neighbouring the clinostatite fragment originally contained manganoan dolo-

mite, which subsequently decomposed and reacted to form manganian augite. However, this does not account for the enrichment of the augite in Cr.

Alternatively, the opaque matrix that contributed Ca, Mn and Cr to form augite might have been more highly reduced than at present. The augite could have formed at high temperature when most of the iron in the opaque matrix was present as metal. This would have been true of Cr also; metal in Tieschitz commonly has < 2000 ppm Cr (Bevan and Axon, 1980), and there is evidence that some Cr was expelled from metal and oxidized to form chromite. Likewise, there is an association of phosphate with metal in the meteorite, the interpretation being that P expelled from metal was oxidized to form phosphate. Thus there is independent evidence that the Tieschitz assemblage is now more oxidized than it was at the time of accretion. It is therefore possible that opaque matrix could originally have been highly reduced with MnO/FeO near 0.4. If this had been the case, Cr would have been distributed between sulphide, metal and silicate as in the enstatite chondrites (Keil, 1968). It is suggested, then, that the augite formed by partially replacing a protoenstatite or clinoenstatite xenocryst, by reaction with highly reduced opaque matrix into which it had been emplaced.

#### The temperature at which the manganian augite grew

Two-pyroxene thermometry has been based on elemental distribution between orthopyroxene and a Ca-pyroxene (see e.g. Lindsley and Andersen, 1983), so cannot be applied directly to the present case in which very low-Ca 'clinoenstatite' is associated with manganian augite; experimental data do not exist. However, we can obtain some information from the individual phases.

The clinoenstatite probably was not formed by the effect of stress on orthoenstatite which, in the Fe-free system, when crystallized from a melt, normally contains more CaO than the 0.22 wt.% now present in the twinned crystal (Biggar, 1985, Fig. 6). Most likely it formed by inversion of protoenstatite precipitated by a chondrule liquid at a temperature of perhaps 1350 °C. Such an inversion could have taken place at room temperature but afterwards the clinoenstatite so produced could not have been heated at intermediate temperatures; clino lamellae in orthobronzite are largely annealed out over one week at 800 °C (Ashworth *et al.*, 1984). Thus, reheating at 'metamorphic' temperatures would have caused the clinoenstatite to transform to the ortho form. It is therefore suggested that the manganian augite overgrowth formed at even higher temperature.

The composition of the augite becomes 'Wo' 0.292, 'En' 0.556, 'Fs' 0.152 when recast according to the convention of Lindsley and Andersen (1983), suggesting that the mineral formed at 1250 °C. There is considerable uncertainty over this estimate, first because the solvus from which it is derived is between orthopyroxene and Ca-rich pyroxene. We may speculate that because the low-Ca pyroxene is monoclinic with very low Ca, partition of Ca into the augite might have been enhanced, in which case the estimated temperature would be a minimum. The second cause of uncertainty is based on the assumption that Mn substitutes only for Fe, but if it substitutes partly for Ca the estimated temperature will be a maximum. Because the two effects are counteractive, the estimated temperature may not be inaccurate. It is within the range of crystallization of chondrule liquids (Gooding and Keil, 1981) which on rapid cooling yield cores of twinned very low-Ca pyroxene with augite rims (Ashworth, 1981; Hutchison *et al.*, 1980).

#### The source of heat

It was argued that clinoenstatite core and manganian augite overgrowth formed in different chemical environments. However, transport of the clinoenstatite between them need not have been accompanied by cooling, the opaque matrix possibly having adhered to the crystal fragment when both were hot. If this were all that was necessary to produce reaction, then evidence of reaction between mafic minerals of chondrules and their opaque rims should be widely and readily observable. That this is not so suggests that some unusual factor was required. It is proposed that the association of the pyroxenes and opaque matrix in question within the largest area of 'white' matrix observed may not be merely coincidental. Hutchison *et al.* (1979) argued that white matrix probably represents nepheline- and albite-normative liquids expressed from deformed and partly crystalline chondrules, and that the liquids finally crystallized at a temperature close to the minimum on the nepheline-albite join, 1068 °C. Cooling and crystallization of the large patch of white matrix could temporarily have produced temperatures in the range estimated for the formation of the manganian augite. Furthermore, augite is stable in the presence of both undersaturated and oversaturated silicates, so white matrix, opaque matrix and clinoenstatite may all have taken part in the reaction.

It cannot be proved that the manganian augite formed *in situ* and so it could have formed elsewhere by an undeterminable source of heat. However, the

hypothesis outlined above, that the manganoan augite formed by reaction between reduced opaque matrix and very low-Ca pyroxene utilising heat from the crystallization of undersaturated liquid, is self consistent. It also is consistent with the hypothesis of Hutchison *et al.* (1979) that Tieschitz accreted hot.

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