MINERALOGICAL MAGAZINE, DECEMBER 1979, VOL. 43, PP. 535-8

Two kinds of exsolution in chondritic olivine

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SUMMARY. Transmission electron microscopy of several chondritic meteorites reveals exsolution products of two kinds in olivine. The coarser variety comprises particles that have nucleated heterogeneously on subgrain boundaries. Electron microprobe data confirm that these are chromite. The second variety, consisting of smaller precipitates distributed randomly, is interpreted as a homogeneously nucleated analogue of the first. It is potentially important as an indicator of cooling history. The aluminium-poor compositions of heterogeneously exsolved chromites suggest that some Cr may have entered tetrahedral sites in olivine during initial rapid crystallization from the melt.

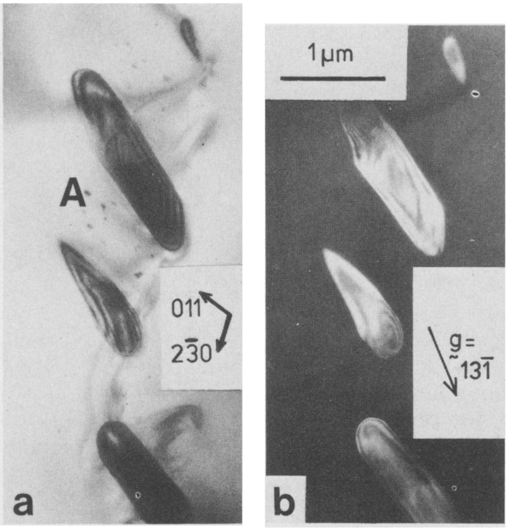
EXSOLUTION of chromite and magnetite has been reported in some terrestrial olivines (Deer *et al.*, 1962; Arai, 1978), and chromium-rich exsolved symplectites have been described from lunar olivines (Bell *et al.*, 1975). Among chondritic meteorites, in the very unequilibrated Type 3 (so termed by Van Schmus and Wood, 1967) olivine sometimes contains appreciable chromium, while this element seems to have been 'expelled' from the olivine of the more equilibrated Types 4-6 (Dodd, 1973). Rather large, evenly distributed chromite particles in some chondritic olivines have been attributed to exsolution (Ramdohr, 1973). The present paper reports the presence of similar, but finer-grained precipitates (exsolved particles) in several ordinary chondrites. The observations were made, by high-voltage transmission electron microscopy, during a study of chondrites belonging to the H chemical group. Two kinds of precipitate were found to be abundant in several relatively equilibrated meteorites of this group. The meteorites studied, their Van Schmus-Wood classifications, and their British Museum (Natural History) catalogue numbers are: Quenggouk, H4, BM 33764; Beaver Creek, H4, BM 73646; Allegan, H5, BM 1920, 281; and Butsura, H6, BM 34795.

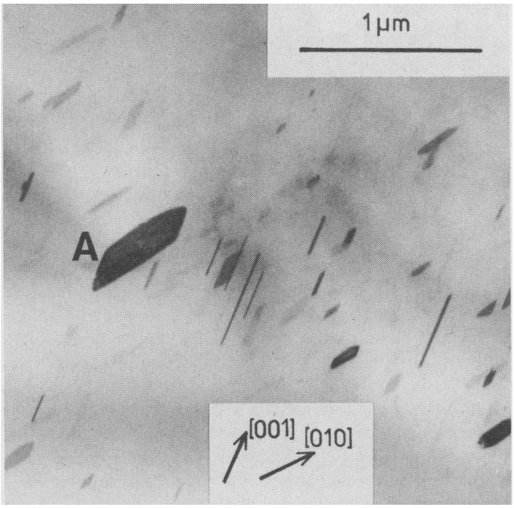
The two kinds of precipitate are: localized trails of particles, mostly rather coarse, associated with arrays of dislocations in the olivine (fig. 1), and a fine variety disseminated through the olivine, which occurs often in the complete absence of dislocations (fig. 2). The coarse variety can often be detected optically in thin-section, as curved trails of dark inclusions. These appear to be the 'swarms along healed cracks' mentioned by Dodd (1969, p. 167 and fig. 8). In the electron microscope, the particles are seen to be crystals, rather regularly spaced, 'decorating' arrays of dislocations (fig. 1). Different, smaller particles are sometimes also visible (e.g. at A in fig. 1*a*). Strictly, the dislocation arrays are subgrain boundaries, rather than healed fractures. Though some may have been introduced by deformation, widely-spaced subgrain boundaries in the olivine phenocrysts of chondrules are likely to have been incorporated during crystal growth.

Adjacent large particles along a subgrain boundary have the same lattice orientation (fig. 1*b*). Electron diffraction patterns show that they have the spinel structure and are topotactically related to the olivine. The topotactic relation is $a_{\mathrm{ol}} // [111]_{\mathrm{sp}}$; $b_{\mathrm{ol}} // \pm[\bar{1}\bar{1}2]_{\mathrm{sp}}$; $c_{\mathrm{ol}} // \pm[1\bar{1}0]_{\mathrm{sp}}$, the same as that observed by Champness (1970) for a magnetite-like spinel produced in olivine by experimental oxidation. The topotaxy is governed by the nearly close-packed oxygen framework of both minerals (Champness, 1970). The particles do not show good crystal form (fig. 1), their shape presumably being determined by local stresses within the subgrain boundary, though they tend to be plate-like in $\{111\}$ planes of the spinel structure. Misfit dislocations can often be seen in the interface with the olivine. An estimate of the cell parameter from electron diffraction patterns, using the host olivine as 'internal standard', is $a = 8.308 \pm 0.033$ Å.

The other kind of precipitate is finer-grained, and occurs away from subgrain boundaries (fig. 2). Particles vary between rod-like and plate-like, with a variety of elongation directions of which two common ones are [010] and [001] of the host olivine. The least fine-grained groups of particles, found in Allegan (fig. 2) and Butsura, have given diffraction patterns indicating the spinel structure in the usual topotactic relation to the olivine, and consistent with the same cell parameter as for the subgrain-boundary precipitates.

These two different occurrences of spinel-like





FIGS. 1 and 2. Transmission electron micrographs at 1 MeV, of exsolved particles in olivine in the Allegan meteorite. FIG. 1 (*left*). A decorated subgrain boundary. (*a*) bright-field, viewed approximately down zone axis [32$\bar{2}$] of the olivine. Small particles are visible between the large ones, for example at A. (*b*) dark-field with diffraction vector $\mathbf{g} = 13\bar{1}$ of the spinel structure, so that only the particles with this structure appear bright. FIG. 2 (*right*). Homogeneously exsolved particles. Bright field. The relatively large particle A shows contrast attributed to misfit dislocations in the boundary with the host olivine. The latter is viewed approximately down zone axis [327]; the projected directions of [010] and [001] of olivine are indicated.

precipitate are interpreted as resulting from exsolution of the same components by two different mechanisms. The particles decorating the subgrain boundaries have nucleated heterogeneously at these special sites, where the pre-existing dislocation array could accommodate some of the strain at the boundaries of the spinel. The small, dispersed particles, on the other hand, represent homogeneous or 'random volume' nucleation (Yund and McCallister, 1970, p. 10) in regions where there were no dislocations.

The composition of the large, heterogeneous precipitates can be estimated. They are too small for individual microprobe analysis, but spot analyses along decorated subgrain boundaries showed a linear covariation in apparent concentrations of elements, which were extrapolated to zero Si prior to ZAF correction, giving the results in Table I. Each olivine analysis in Table I is the average of six determinations within one grain which was host to the precipitates. Neither olivine was significantly zoned. The Allegan olivine is $Fo_{82.7}Fa_{17.3}$ and the Quenggouk grain $Fo_{81.4}Fa_{18.6}$; these are normal compositions for equilibrated H-group olivines (Van Schmus, 1969). The estimated precipitate compositions are liable to errors due to fluorescence effects across the boundary with olivine (Reed and Long, 1963), but these are probably minor since linear variation was observed between areas with zero and 30% precipitate in the Allegan grain. The Quenggouk estimate is less good because all analyses contained less than 20% precipitate. The MgO estimates are particularly uncertain because of the swamping effect of Mg in host olivine. However, the data are adequate to confirm that the exsolution product is chromite, close to $FeCr_2O_4$ in composition.

The Allegan results indicate between 10 and 20 mole% $(Mg,Fe)Al_2O_4$ and perhaps ferric iron to the extent of a few % of the R^{3+} cations. These

TABLE I. *Electron microprobe data*

Meteorite	Allegan olivine	Precipitate	Quenggouk olivine	Precipitate
SiO_2	40.06		39.17	
TiO_2	0.01	1.0±0.1	0.00	0.7±0.3
Al_2O_3	0.02	6.6±0.5	0.00	5.3±0.5
Cr_2O_3	0.02	57.7±0.5	0.01	56.4±1.5
FeO*	16.29	30.0±0.2	17.67	32.4±3.3
MnO	0.44	1.0±0.1	0.43	1.4±0.3
MgO	43.70	4.4±1.6	43.26	<3
CaO	0.01	<0.2	0.03	
Total	100.55		100.57	

* total Fe as FeO.

results are consistent (Deer *et al.*, 1963) with the cell parameter, estimated above using different grains in the same meteorite. Quantitative analytical data have not been obtained for the even smaller homogeneous precipitates. In a transmission electron microscope fitted with energy-dispersive X-ray analyser, when the beam was centred on a cluster of these particles, Cr was detected, whereas it was below the detection limit in adjacent clear olivine.

The chemistry of the homogeneous process cannot be discussed in detail, but the data for the heterogeneous precipitates may bear on the crystal chemistry of chondritic olivine. Chromite is presumably a stable product of the breakdown of chromium-bearing olivine: coarse chromite of similar composition is a member of the stable mineral assemblage in equilibrated H chondrites (Bunch *et al.*, 1967). However, exsolution of chromite from lunar or terrestrial olivine is usually accompanied by exsolution of a silicate (Bell *et al.*, 1975; Arai, 1978). In the present observations, any second exsolution product is very minor in amount (fig. 1; Table I). Symplectites were not observed, whereas they would be expected if the presence of Cr in octahedral co-ordination in the initial olivine was not accompanied by a substitution for Si in tetrahedral sites. For example, if the substitution was $2\,Cr^{3+}$ for $3\,(Mg,Fe)^{2+}$, exsolution of chromite should also produce pyroxene; oxidative exsolution of Cr^{2+} should again produce symplectites (cf. Champness, 1970). The observations thus indicate that a substitution for Si occurs in chondritic olivine. One likely such substitution, proposed by Dodd (1973) on the basis of a correlation between Cr and Al in unequilibrated chondritic olivines, is Al for Si coupled with Cr^{3+} for (Mg,Fe). Exsolution might then be expected to produce a spinel of the composition $(Fe,Mg)CrAlO_4$, much more aluminous than observed here. Alternatively, $FeCr_2O_4$ might be exsolved while the Al was merely redistributed between tetrahedral and octahedral sites in the host, as seems to have happened during exsolution of spinel from a pyroxene (Okamura *et al.*, 1976); however, the residual Al is not obvious, this element being barely detectable in the host olivines (Table I). The data are not conclusive, but raise the possibility that some Cr^{3+}, despite its preference for octahedral co-ordination (Dodd *et al.*, 1975), was accommodated in tetrahedral sites by the substitution of $2Cr^{3+}$ for (Mg,Fe)Si, during rapid crystallization of chondrule olivine from the melt.

The homogeneous exsolution phenomenon is particularly interesting, as a potential indicator of the history of cooling through a range of high temperatures. In principle, such a particle distribution, free from the interfering effects of irreproducible heterogeneities, is amenable to experimental study and to application of the kinetic theory of nucleation and growth (Yund and McCallister, 1970). Its discovery is particularly valuable in these chondrites, where the pyroxenes lack fine-scale exsolution effects. In Type 3 chondrites the calcium-bearing pyroxenes usually have fine exsolution substructures indicating rather rapid cooling (Ashworth and Barber, 1977), which are not found in the pyroxenes (orthopyroxene and diopsidic clinopyroxene) of the chondrites under discussion. Their absence reflects a more protracted high-temperature history, but the present results show that this history was transient enough for precipitates in olivine to remain small. The exsolution product is much less coarse than in the terrestrial peridotite studied by Arai (1978). On the other hand, Dodd *et al.* (1975) specifically remark on the absence of any exsolution in the olivine of a rapidly-cooled inclusion in the meteorite St. Mesmin, whose high Cr content is admittedly regarded as mostly Cr^{2+}. In the present study, homogeneous exsolution has not been noticed in Type 3 chondrites, though the decorated subgrain boundaries do occur in these (cf. Dodd, 1969, fig. 8). The closest lunar analogy appears to be the 'Type F symplectites' which occur in mare basalts, and may not be symplectites at all (Bell *et al.*, 1975, p. 239). Within the suite of meteorites studied, there is a suggestion of systematic variation in the size of the homogeneously exsolved particles. In Quenggouk and Beaver Creek the particles are generally ~ 10–100 nm long, whereas in Allegan (fig. 2) and Butsura they are often ~ 1 μm long. This difference is consistent with the more equilibrated nature of the Type 5 and 6 meteorites than the Type 4, but the very fine scale of exsolution in all cases underlines the incompleteness of metamorphic reconstitution in the H chondrites, even in material belonging to Type 6.

Acknowledgements. The specimens form part of the H-group consortium suite supplied by Dr R. Hutchison (British Museum, Natural History). This work is supported by the NERC. I thank Dr M. H. Loretto (Birmingham University) for the use of the high-voltage electron microscope, and Dr S. Murphy and colleagues (Department of Metallurgy and Materials, Aston) for microanalysis facilities. I am grateful to Professor D. J. Barber for helpful discussions.

REFERENCES

Arai (S.), 1978. Chromian spinel lamellae in olivine from the Isanai-Dake peridotite mass, Hokkaido, Japan. *Earth Planet. Sci. Lett.* **39**, 267–73.

Ashworth (J. R.) and Barber (D. J.), 1977. Electron microscopy of some stony meteorites. *Phil. Trans. R. Soc. Lond.* **A 286**, 493–506.

Bell (P. M.), Mao (H. K.), Roedder (E.), and Weiblen (P. W.), 1975. The problem of the origin of symplectites in olivine-bearing lunar rocks. *Proc. 6th Lunar Sci. Conf.* **1,** 231-48.

Bunch (T. E.), Keil (K.), and Snetsinger (K. G.), 1967. Chromite composition in relation to chemistry and texture of ordinary chondrites. *Geochim. Cosmochim. Acta,* **31,** 1569-82.

Champness (P. E.), 1970. Nucleation and growth of iron oxides in olivines, $(Mg,Fe)_2SiO_4$. *Mineral. Mag.* **37,** 790-800.

Deer (W. A.), Howie (R. A.), and Zussman (J.), 1962. *Rock-forming Minerals,* **1,** 5-6. London, Longmans.

———— 1963. *Rock-forming Minerals,* **5,** fig. 6. London, Longmans.

Dodd (R. T.), 1969. Metamorphism of the ordinary chondrites: A review. *Geochim. Cosmochim. Acta,* **33,** 161-203.

—— 1973. Minor element abundances in olivines of the Sharps (H-3) chondrite. *Contrib. Mineral. Petrol.* **42,** 159-67.

——Morrison-Smith (D. J.), and Heyse (J. V.), 1975. Chromium-bearing olivine in the St. Mesmin chondrite. *Geochim. Cosmochim. Acta,* **39,** 1621-7.

Okamura (F. P.), McCallum (I. S.), Stroh (J. M.), and Ghose (S.), 1976. Pyroxene-spinel intergrowths in lunar and terrestrial pyroxenes. *Proc. 7th Lunar Sci. Conf.* **2,** 1889-99.

Ramdohr (P.), 1973. *The Opaque Minerals in Stony Meteorites,* 47. Amsterdam, Elsevier.

Reed (S. J. B.) and Long (J. V. P.), 1963. Electron-probe measurements near phase boundaries. In *X-ray optics and X-ray microanalysis.* Eds. V. E. Cosslett and A. Engström. New York, Academic Press.

Van Schmus (W. R.), 1969. The mineralogy and petrology of chondritic meteorites. *Earth Sci. Rev.* **5,** 145-84.

—— and Wood (J. A.), 1967. A chemical-petrologic classification for the chondritic meteorites. *Geochim. Cosmochim. Acta,* **31,** 747-65.

Yund (R. A.) and McCallister (R. H.), 1970. Kinetics and mechanism of exsolution. *Chem. Geol.* **6,** 5-30.

[*Manuscript received 9 May 1979;
revised 4 June 1979*]