

USTÍ NAD ORLICI: A NEW L6 CHONDRITE FROM CZECHOSLOVAKIA

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Ustí nad Orlicí (Kerhartice), a meteorite which fell on June 12, 1963 in Czechoslovakia, is classified as a L6 chondrite. Compositions of olivine (Fa 23.4), orthopyroxene (Fs 20, Wo 1.3), plagioclase ($Ab_{88}An_{10}Or_3$) along with the bulk composition of the meteorite support this classification. Chromite compositions vary with grain size. Large chromites are higher in TiO_2 and lower in Fe^3 than small chromites. This may indicate that either these two chromites formed initially under different fO_2 conditions, or that this difference resulted from different equilibration behaviors of both chromites as a function of grain size. The meteorite contains three distinct sulfide assemblages: 1) troilite-pentlandite, 2) troilite, pentlandite-cubanite-chalcopyrite-pyrrhotite-mackinawite, 3) troilite-tetrataenite-(Fe, Cu, Ni) $_{1.02}S$. These assemblages indicate equilibration down to temperatures close to 200 °C.

INTRODUCTION

On June 12, 1963 at 1:58 p.m. a stony meteorite fell into the garden of house No. 20 in the village of Kerhartice near Ustí nad Orlicí (49°58'30"N latitude, 16°22'30"E longitude) in Czechoslovakia. The event was registered by one station of the meteor registration network of the Astronomical Observatory in Ondřejov.

One piece of the meteorite, a distorted tetrahedron with a complete, well developed brownish to black glassy fusion crust, weighed 1260 g at the time of its recovery. An illustrated description of the uncut stone was given by K. Tuček (1963). The meteorite is listed under No. 397 in the meteorite collection of the National Museum in Prague, Czechoslovakia. This is the first chemical and petrological study of the meteorite.

A freshly cut slab revealed that the Ustí stone is well crystallized and almost glass-free. The meteorite consists of 81.3% silicates (olivine, pyroxenes, feldspars+phosphates), 9.9% metals, 8% troilite, and 0.8% chromite (and ilmenite) by weight. Numerous well-developed porphyritic, olivine-barred and fan-shaped chondrules occur in the well crystallized matrix. Plagioclase feldspar usually fill the interstices between the well crystallized olivine and pyroxenes (Fig. 1).

Three polished thin sections were prepared for petrographic and electron microprobe analyses of individual minerals. An additional piece of 1 g was also selected for chemical analyses.

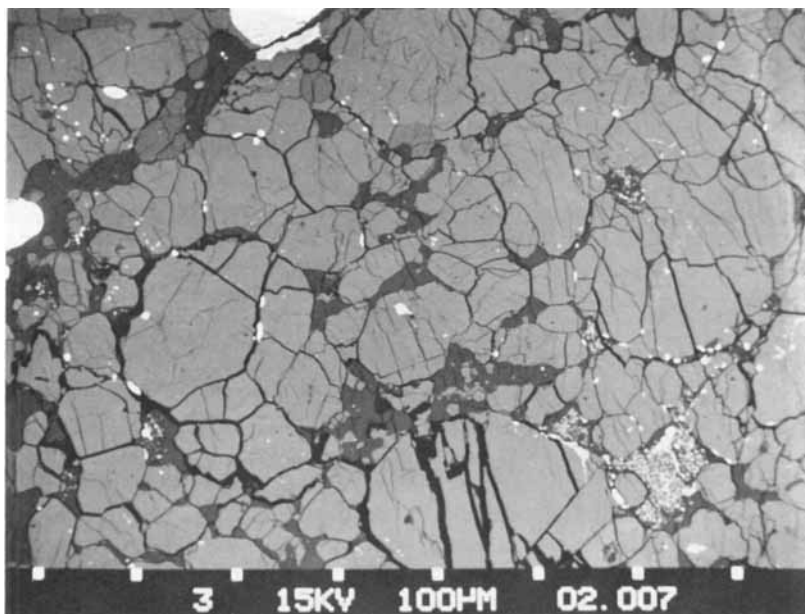


Fig. 1 SEM view of a polished thin section of the Ustí nad Orlicí L6 chondrite displaying the well crystallized nature of the meteorite. Light gray olivine and pyroxene, dark gray plagioclase, white chromite, troilite and metal.

CHEMISTRY

The bulk composition was determined by XRF (Norrish and Hutton, 1968) and neutron activation analysis on the silicate and metal fractions. The results are shown in Table 1.

Although the bulk chemical data are entirely consistent with the average L chondrite values (Mason, 1979), it is noteworthy that the metal content and total iron are relatively high, which would place Ustí nad Orlicí in the vicinity of the H group chondrites. On the other hand, it exhibits a relatively high degree of oxidation within the L group and a low Ni/Si ratio which points to the opposite direction of the oxidation state fractionation (Müller *et al.*, 1971). In this respect it resembles the Madiun L6 chondrite (Reid and Fredriksson, 1982).

PETROGRAPHY AND MINERAL COMPOSITION

The well crystallized nature of the meteorite places it clearly in the 5-6 petrologic group of Van Schmus and Wood (1967). Minerals encountered in chondrules and matrix are olivine, orthopyroxene, clinopyroxene, plagioclase, kamacite, taenite, tetrataenite, troilite, chromite, and ilmenite. Numerous troilite grains in the matrix were found to contain irregular pentlandite inclusions. Two additional sulfide bearing assemblages were also encountered: 1) troilite-tetrataenite-kamacite-native copper and a copper iron sulfide, 2) pentlandite-mackinawite-cubanite-troilite-chalcopyrite. Nickeliferous pyrrhotite also occurs as inclusions in pentlandite grains of the last assemblage. Numerous

Table 1
Chemical composition of the Ustí nad Orlicí chondrite

weight %		ppm		mode in weight %	
SiO ₂	38.1	Sc	8.90	Silicates	81.3
Al ₂ O ₃	1.82	Cu	125	Metal	9.9
FeO	13.2	Zn	56	Troilite	8
FeS	8	As	4.2	Chromite	0.8
Fe _{met}	8.8	Se	10.8		
MgO	24.7	La	0.31		
CaO	1.75	Eu	0.095	$\frac{\text{FeO}}{\text{FeO} + \text{MgO}} = 23 \text{ mole \%}$	
Na ₂ O	0.887	Ir	0.427		
K ₂ O	0.087	Au	0.179		
MnO	0.323				
Cr ₂ O ₃	0.525				
Ni	1.10				
Co	0.067				
Sum	99.36				
Fe _{tot.}	24.0				

pockets of a unique kind of mesostasis were found in the groundmass. This mesostasis consists of plagioclase, chromite, and whitlockite.

Numerous electron probe microanalyses were carried out on the individual mineral grains in order to trace the history of formation.

Olivine compositions display a very narrow range from 22.2% to 24.4% fayalite content with an average of 23.4% Fa (Fig. 2). These compositions fall very well within the range of the L group.

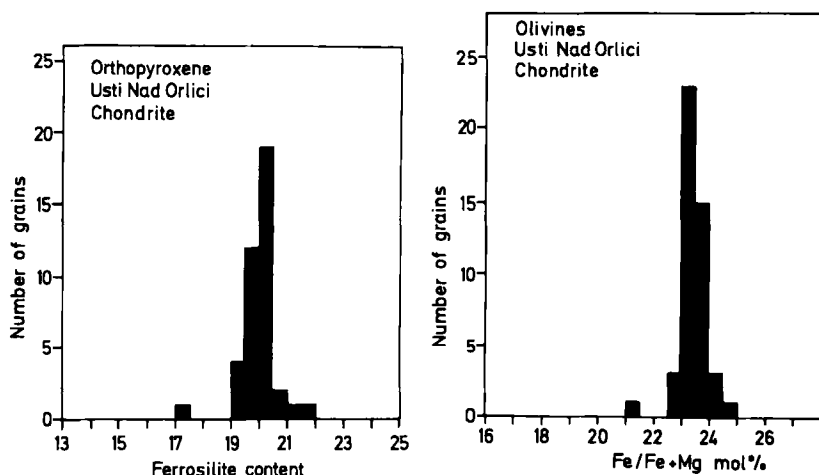


Fig. 2 Histograms showing the orthopyroxene and olivine compositions.

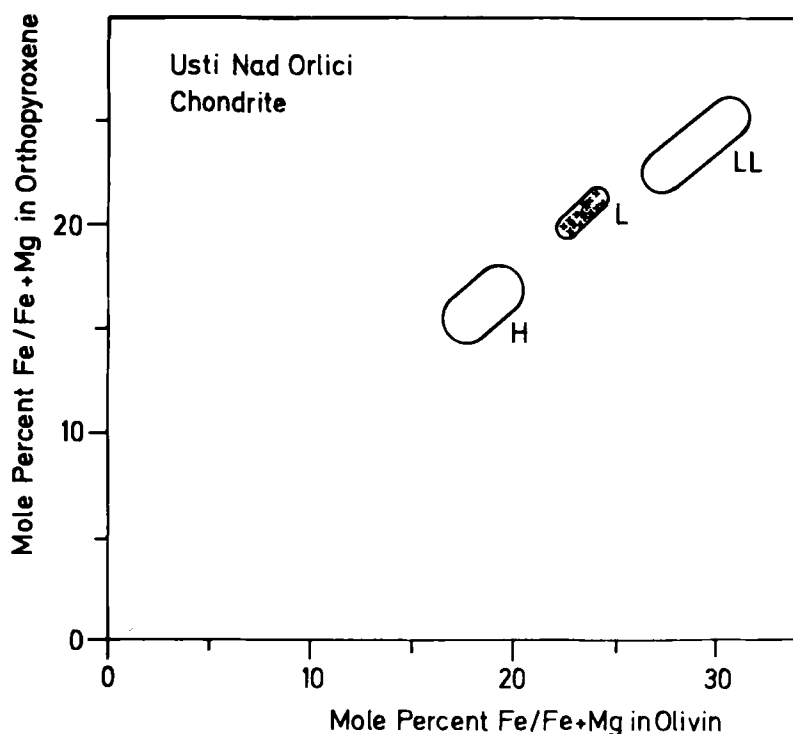


Fig. 3 $\text{Fe}/\text{Fe}+\text{Mg}$ in orthopyroxene versus $\text{Fe}/\text{Fe}+\text{Mg}$ in olivine. The values fall within the L field.

The compositions of orthopyroxenes range from 19.2 to 21.2 ferrosilite with an average of 20% Fs (Fig. 2). Figure 3 shows the $\frac{\text{Fe}}{\text{Fe}+\text{Mg}}$ in pyroxene versus $\frac{\text{Fe}}{\text{Fe}+\text{Mg}}$ in olivine as compared to the ranges for H-, L-, and LL-groups. The measured values plot perfectly in the L-field. Average olivine, orthopyroxene and clinopyroxene compositions are given in Table 2. Plagioclase compositions display also a very narrow compositional range (Fig. 4) with an average of $\text{Ab}_{85}\text{Or}_5$. These chemical features of the individual silicates allow a clear cut classification of Ustí as belonging to the L6 petrologic group.

A study of the minerals may indicate that the features encountered in Ustí nad Orlici are not unusual compared to other L6 chondrites. A careful study of chromite, ilmenite, sulfides, and tetrataenite-bearing assemblages revealed, however, that these opaque phases may store important information relevant to the formational history of the meteorite.

Chromite was found to occur in various modes of intergrowth. The major part is present as coarse anhedral grains, however, with idiomorphic boundaries when adjacent to troilite or metal (Fig. 5). It is also present as small idiomorphic grains enclosed in olivine or pyroxene (Fig. 6). Another rare but unique type of chromite was encountered together with plagioclase feldspar and whitlockite (and sometimes apatite). The three minerals form an intimate intergrowth as pockets between olivine and pyroxene grains. Chromite occurs always as fine grains either dispersed in numerous plagioclase grains

Table 2
Composition of olivine, pyroxene, whitlockite and ilmenite
(average of several analyses) in Ustí nad Orlicí chondrite (in wt. %)

	Olivine	Orthopyroxene	Clinopyroxene	Whitlockite	Ilmenite
SiO ₂	38.2	54.7	54.0	n.d.	0.11
TiO ₂	0.02	0.19	0.47	n.d.	52.6
Al ₂ O ₃	0.10	0.23	0.60	n.d.	0.35
Cr ₂ O ₃	0.05	0.15	0.88	n.d.	0.11
V ₂ O ₃	n.d.*	n.d.*	n.d.	n.d.	n.d.
FeO	21.6	13.4	4.73	0.40	34.9
MgO	39.4	29.4	16.7	3.18	3.08
MnO	0.43	0.47	0.24	n.d.	9.13
CaO	0.01	0.63	21.5	47.0	n.d.
K ₂ O	n.d.	n.d.	0.47	n.d.	n.d.
Na ₂ O	n.d.	n.d.	n.d.	2.66	n.d.
P ₂ O ₅	n.d.	n.d.	n.d.	46.4	n.d.
Cl	n.d.	n.d.	n.d.	n.d.	n.d.
F	n.d.	n.d.	n.d.	n.d.	n.d.
Totals	99.81	99.17	99.59	99.64	100.28
	Fa: 23.5	Fs: 20	Wo: 48		
			Fs: 7.6		
			En: 44.4		

*n.d. = not detected

which occupy the cores of the pockets (Fig. 7) or as oriented distorted laths along two directions in plagioclase (Fig. 7). Whitlockite usually is aligned along the boundaries of these pockets to the surrounding olivine and pyroxenes. This mode of occurrence was also observed by Ramdohr (1973) who called it "Haufenchromit," however, without recording the whitlockite. This assemblage is enriched in the incompatible elements K, P, Cl, and REE and hence we believe it is a new type of mesostasis typical of chondritic meteorites. It is not restricted to Ustí nad Orlicí or the L group since a survey of LL- and H-group revealed that this mesostasis is also present in other ordinary chondrites, regardless of the petrologic group. The high concentration of chromite in this complex assemblage indicates that chondritic mesostasis contrasts sharply in its composition with lunar and terrestrial mesostasis due to the high Cr-content. The composition of plagioclase in the mesostasis falls within the range shown in Figure 4. Whitlockite was found to be barren of Cl and F and to contain an average Na₂O content of 2.75% (Table 2).

The chromite analyses revealed a distinct relationship between the chemistry of chromites and the mode of occurrence. Large chromite grains are usually characterized by high TiO₂-content (> 3%), whereas the small ones are lower in TiO₂ (< 2.25%). Gradations in size and chemistry between the two types are the rule. Many interesting

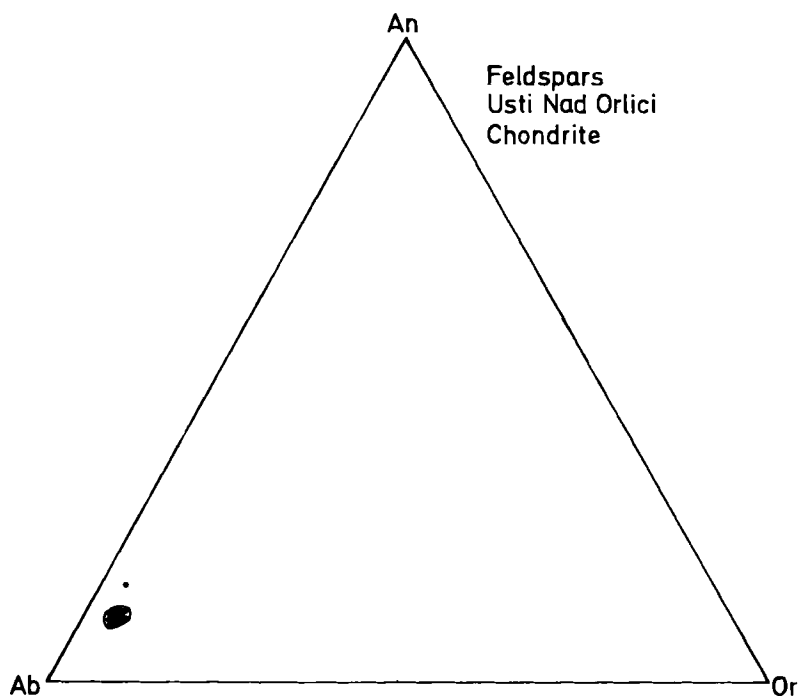


Fig. 4 Compositions of plagioclase in the An Ab Or compositional diagram.

features emerge from the cationic relationships of divalent, trivalent, and tetravalent cations of the analyzed chromites.

The Al/Cr ratios of chromites indicate no Al:Cr substitutional relationship regardless of the chromite type (Fig. 8). The data points spread horizontally between 1/5 and 1/6 ratios. It seems that these two elements are sympathetically related and perhaps involved in a coupled substitution. This behavior is distinctly different from the substitutional relationships of Cr and Al in magmatic rocks, lunar or terrestrial, and indicates that such magmatic processes were not responsible for these elemental relationships.

The amount of Fe^{3+} is directly related to the TiO_2 content of chromite. $\text{Cr}^{3+} + \text{Al}^{3+} + \text{V}^{3+}$ versus Ti^{4+} clearly reflects this feature (Fig. 9). All data points plot below the 8/16 stoichiometric line along a slope steeper than the 8/16 line. The high Ti chromites are close to the stoichiometric line. The deviation from the line increases upon decrease of TiO_2 content. This behavior is also reflected in the $\text{Ti}^{4+}/\text{Fe}^{3+}$ plot. The lower the Ti content the higher the Fe^{3+} in chromite (Fig. 10). This indicates that the small chromites were formed under higher $f\text{O}_2$ conditions than the large chromites. Very probably Ti^{4+} is substituting for Cr^{3+} , Al^{3+} , and Fe^{3+} in a complex coupled substitution.

The $\text{Fe}^{2+}/\text{Mg}^{2+}$ substitutional relationship indicates also that the TiO_2 content of chromite is a controlling factor (Fig. 11). The substitutional relationship for TiO_2 -poor chromites displays a steeper slope than for the TiO_2 -rich chromites. Between these two slopes a big number of fan-shaped slopes could be plotted connecting chromites with the same intermediate TiO_2 contents. This is exactly the inverse relationship compared to

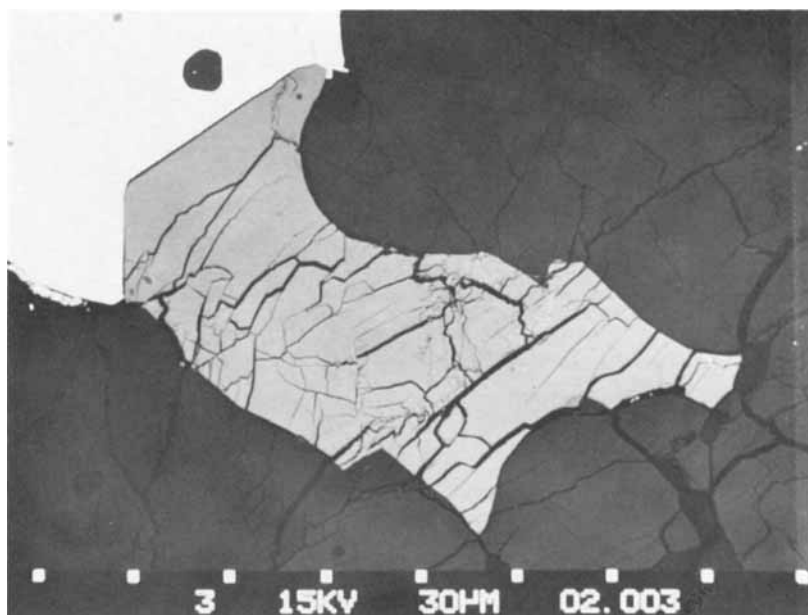


Fig. 5 Coarse Ti-rich chromite (light gray with cracks) enclosed between olivine and orthopyroxene (gray) and with idiomorphic features against troilite (white).

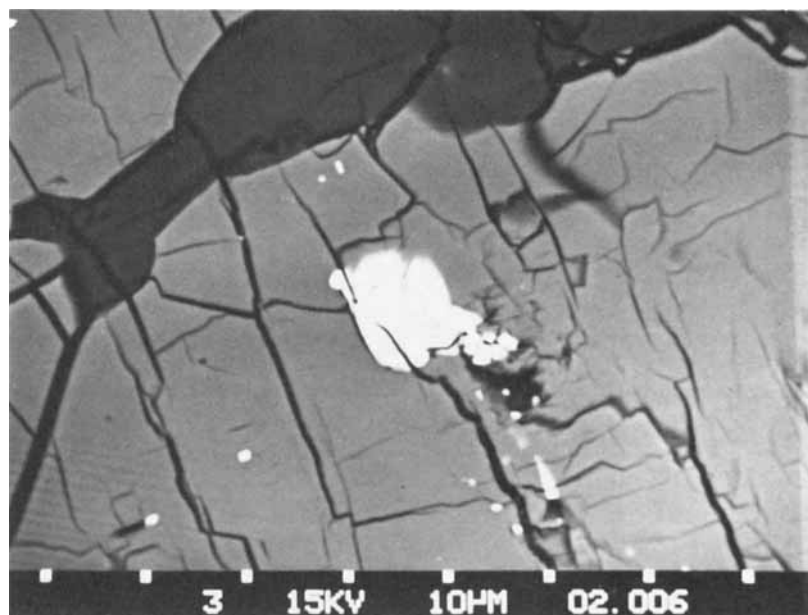


Fig. 6 Inclusions of small Ti-poor chromite (white) in pyroxene (light gray). Dark gray is plagioclase.

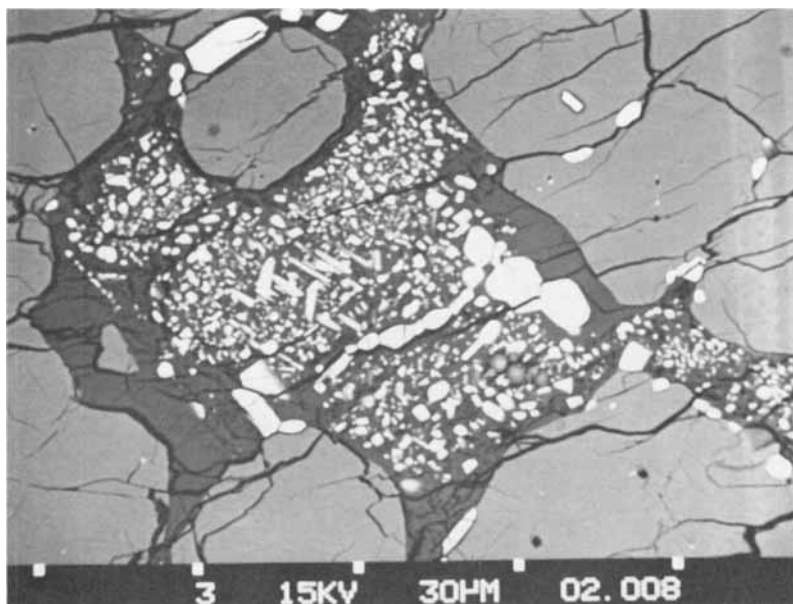


Fig. 7a Meteoritic mesostasis consisting of chromite-plagioclase-whitlockite intergrowth. SEM view.

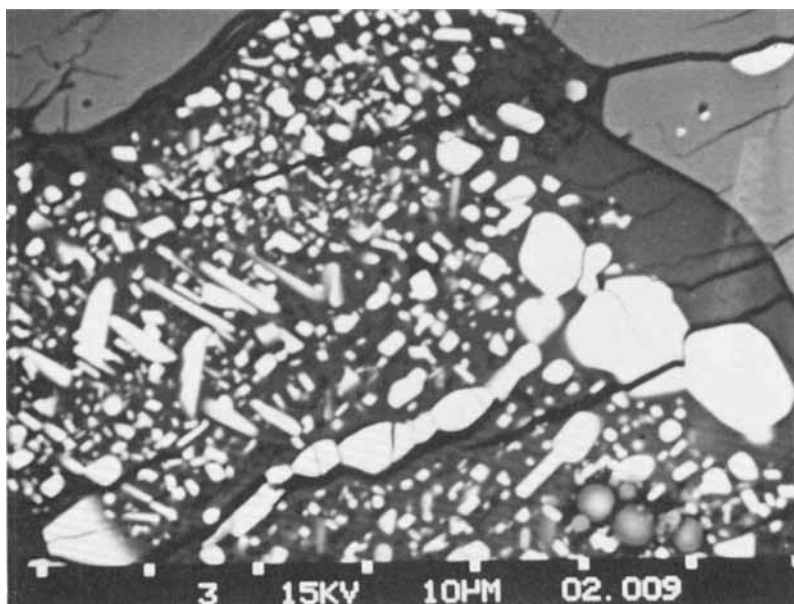


Fig. 7b Detail from 7a showing the oriented chromite (white) plagioclase intergrowth. SEM view.

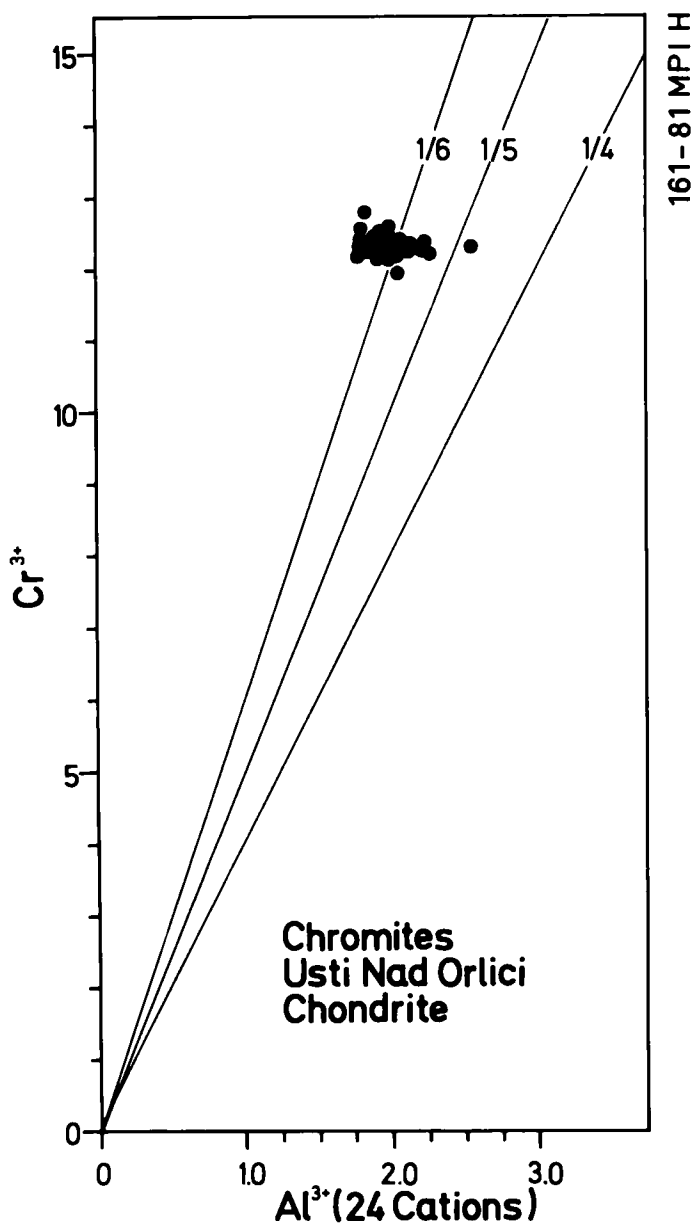


Fig. 8 Cr^{3+}/Al^{3+} in chromites. Note the lack of substitutional relationship.

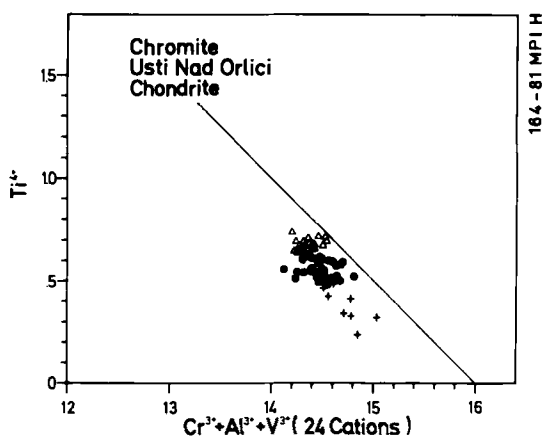


Fig. 9a Ti^{4+} versus $\text{Cr}^{3+} + \text{Al}^{3+} + \text{V}^{3+}$ in chromites. Note the deviation of the data points from the stoichiometric 8:16 line. High Ti-chromites (triangles) show less deviation from the stoichiometric line than Ti-rich chromites (crosses).

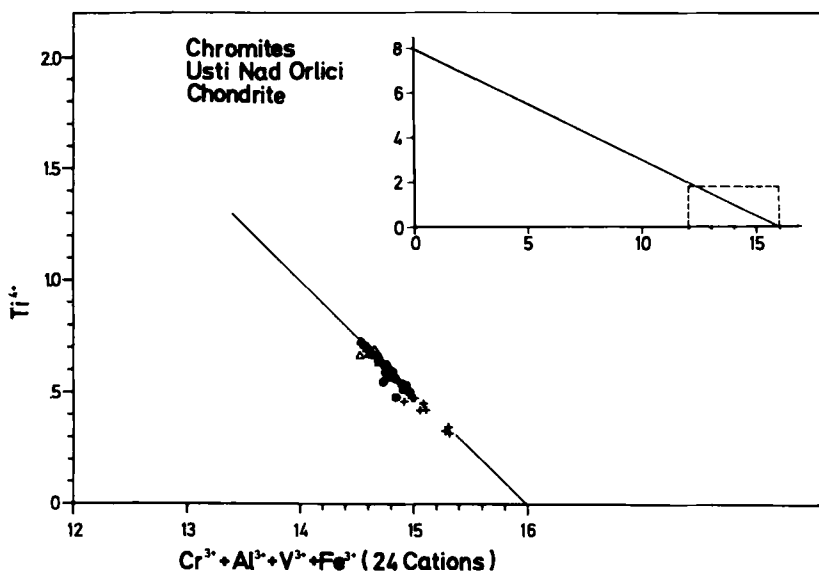


Fig. 9b Ti^{4+} versus $\text{Cr}^{3+} + \text{Al}^{3+} + \text{V}^{3+} + \text{Fe}^{3+}$ in chromites. All points plot in conformity with the 8:16 line.

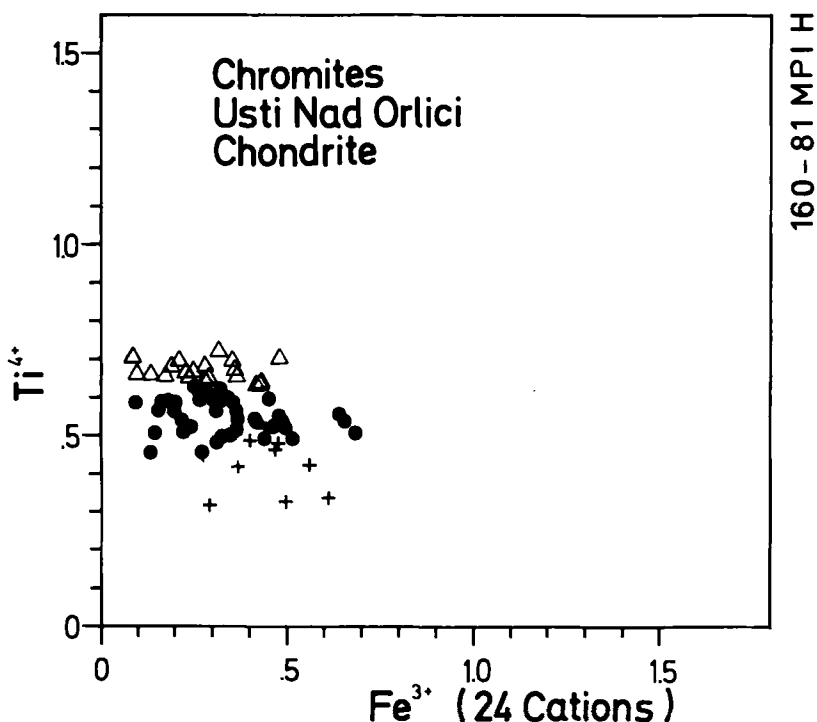


Fig. 10 Ti^{4+} versus Fe^{3+} in chromites. Ti-rich chromites (triangles) show lower Fe^{3+} -content than Ti^{3+} -poor chromites (crosses).

lunar spinels (Haggerty, 1972). The divalent substitutional relationship in lunar spinels indicates steeper slopes for high TiO_2 members than for Cr-rich spinels. Thus, the equilibration processes prevailing during the formation of the Ustí L6 chondrite are distinct from those which took place during the cooling of lunar basalts. The features observed could reflect the primary relationship if chromites did not participate considerably in the equilibration process with the silicates. Then the importance of Ti^{4+} and Fe^{3+} emerges as a sensitive parameter in understanding the history of oxidation during the formation of chondrites before equilibration.

These features could have resulted from one of the following processes: 1) The chemical relationships of Ti-rich and Ti-poor chromites may have been produced during the meteorite formation and did not change during equilibration or 2) the chemical features were produced during equilibration as a result of the different grain sizes of the two chromite types.

For the first alternative the results may then indicate that conditions prevailing during the formation of early Ti-poor chromites were distinctly more oxidizing than during the formation of Ti-rich large chromites. It is noteworthy to mention that large chromites frequently occur with metallic iron or metallic iron + troilite.

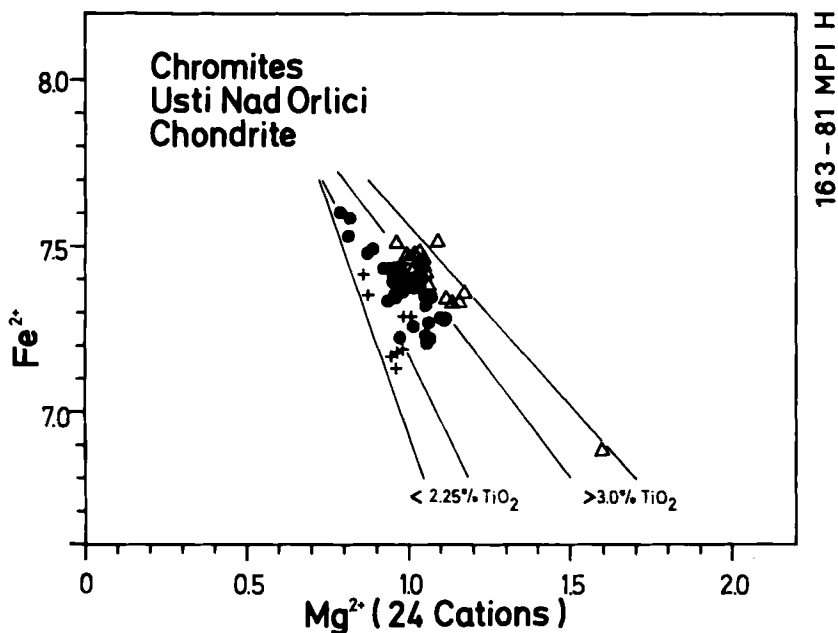


Fig. 11 Fe^{2+} versus Mg^{2+} in chromites. The substitutional ratios for Ti-rich chromites plot on lines with lower slopes than for Ti-poor chromites.

In the case of the second alternative equilibration of small chromites with the coexisting silicates was more efficient than for large chromites. This may suggest that small chromites may have lost TiO^{4+} to pyroxenes and gained Cr^{3+} and Fe^{3+} (and perhaps Al^{3+}) from them during equilibration instead. This may explain why chromites in Ustí do not show any evidence for Al/Cr substitution. The results, however, do not allow a clear cut decision between the proposed mechanisms. A detailed study of the chromites in L- and LL-chondrites may delineate this problem (Yabuki and El Goresy, 1984).

Analyses of ilmenite grains encountered in Ustí nad Orlici indicate an exceptionally high MnO content; the highest ever recorded in a meteoritic ilmenite (9.13%, Table 2).

In addition to the frequent troilite, three sulfide-metal assemblages were also found.

- 1) The first assemblage consists of pentlandite + troilite, or pentlandite + troilite + native copper (Fig. 12).
- 2) The second assemblage is more complex with troilite, pentlandite, pyrrhotite, cubanite, chalcopyrite and mackinawite (Fig. 13). Pentlandite compositions in the two assemblages are different (Tables 3, 4). In the first assemblage pentlandite contains 19.0 wt. % Ni (14.7 atomic %). This is very close to the limit determined experimentally by Misra and Fleet (1972) at temperatures below 300 °C. Pentlandite in the second assemblage has a higher Ni content of 27.6 wt. % (21.4 atomic %) (Table 4). The presence of cubanite, chalcopyrite, mackinawite is interpreted as a strong evidence for the equilibration to very low temperatures not far from 200 °C.

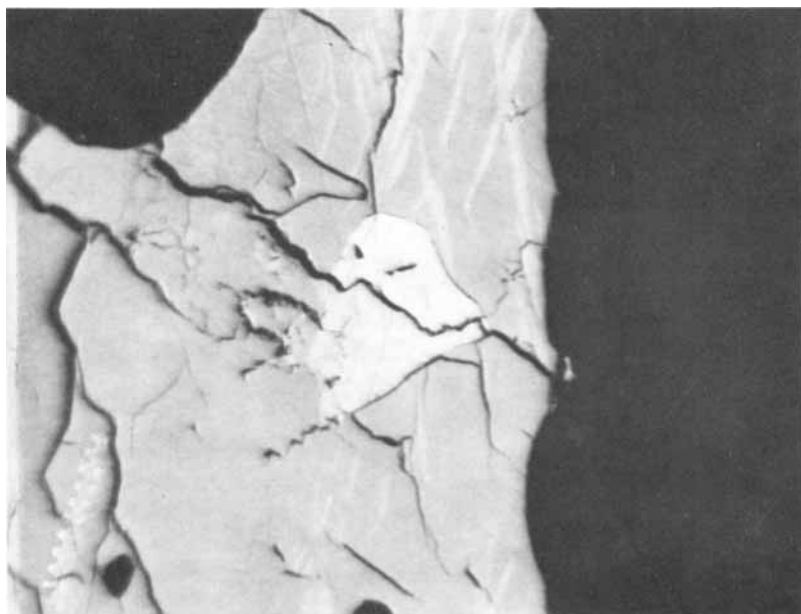


Fig. 12 Pentlandite (white triangular inclusion) in troilite. Note twin lamellae in troilite. Length of Figure: 50 microns.

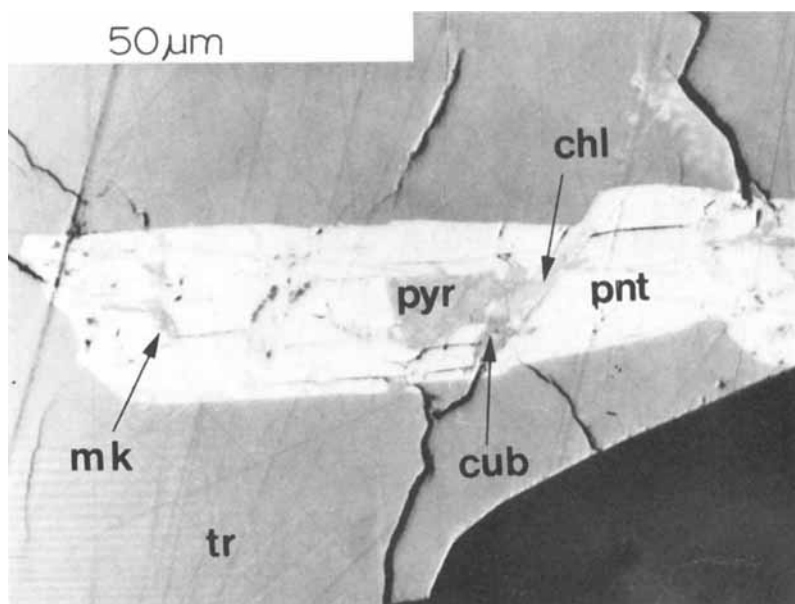


Fig. 13 Photomicrograph of the assemblage troilite (Tr), pentlandite (pnt), pyrrhotite (pyr), cubanite (cub), chalcopyrite (chl), and mackinawite (mk).

Table 3
Composition of sulfide phases and native copper in the first assemblage
in Ustí nad Orlicí chondrite (in wt. %)

	Troilite	Pentlandite	Copper
Fe	62.9	45.7	4.53
Ni	0.13	19.0	1.88
Co	n.d.*	0.75	0.10
Cu	0.13	0.24	94.4
S	<u>36.6</u>	<u>33.3</u>	<u>0.2</u>
Totals	99.76	98.99	101.11
Atoms			
Fe	0.992	6.332	
Ni	—	2.504	
Co	—	0.098	
Cu	—	0.031	
S	<u>1.004</u>	<u>8.035</u>	
Totals	1.996	17.000	

*n.d. = not detected

Table 4
Composition of sulfide phases in the second assemblage
in Ustí nad Orlicí chondrite (in wt. %)

	Troilite	Pyrrhotite	Pentlandite	Cubanite
Fe	63.3	58.5	37.1	38.1
Ni	n.d.*	3.63	27.6	3.04
Co	n.d.	0.07	0.46	0.12
Cu	0.10	0.43	0.33	19.5
S	<u>36.9</u>	<u>35.8</u>	<u>33.5</u>	<u>34.6</u>
Totals	100.3	98.43	98.99	95.36
Atoms				
Fe	0.992	0.938	5.148	1.923
Ni	—	0.055	3.648	0.153
Co	—	0.001	0.063	—
Cu	—	0.006	0.039	0.867
S	<u>1.008</u>	<u>1.000</u>	<u>8.102</u>	<u>3.048</u>
Totals	2.000	2.000	17.000	5.991

*n.d. = not detected

- 3) The third assemblage consists of troilite, tetrataenite, metallic Cu, and an unusual iron, copper, sulfide (Fig. 14). The metal:sulfur ratio in the iron, copper sulfide phase is higher than 1:1 (1.016-1.02) (Table 5). This phase contains more than 1 wt.% Cu and is optically distinct from troilite. It shows a higher reflectivity with a faint olive-green tinge.

More than 95 metal analyses were performed on kamacite and taenite in the three sections prepared. Kamacite displays a very narrow composition ranging between 3 and 4% Ni. In comparison the Ni content of taenite seems to be highly variable between 11 and 59% (Fig. 15). This high variation of Ni in taenite could, however, be an artifact due to the overlap of the electron beam on both kamacite and plessite. Figure 16 shows the Ni/Co ratios of all points measured in the metals. It is quite evident that kamacite shows a higher Co-concentration than taenite and that the Co content of the metal decreases upon increase of Ni, a feature well established in many chondritic metal phases.

CONCLUSIONS

The Ustí nad Orlicí chondrite is classified as a L6 chondrite. This classification is supported by 1) the chemical composition of the meteorite, 2) the composition of the coexisting olivines and orthopyroxenes, and 3) the well crystallized texture of the meteorites. Chromite compositions vary as a function of their grain size and mode of occurrence. Small chromite inclusions are lower in TiO_2 , higher in Fe^{3+} than large xenomorphic chromites. Hence, they are more oxidized than large chromites. The $\text{Fe}^{2+}/\text{Mg}^{2+}$ substitutional relationship of both chromites is also different. Large chromites

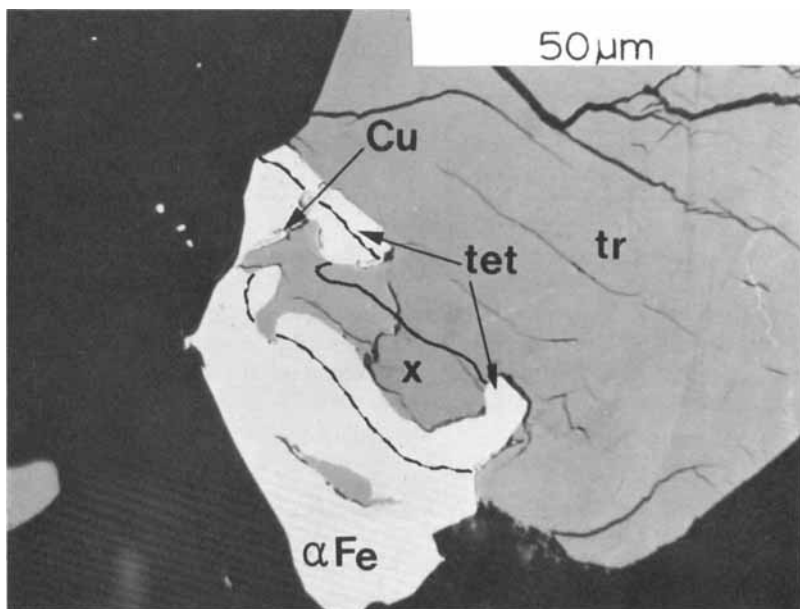


Fig. 14 Photomicrograph of the third assemblage: Troilite (Tr), metallic Cu (Cu), tetrataenite (tet), $(\text{Fe, Cu, Ni})_{1.02}\text{S}$ (x) and kamacite ($\alpha \text{ Fe}$).

Table 5
Composition of sulfides and tetrataenite in the third assemblage
in Ustí nad Orlicí chondrite (in wt. %)

	Troilite	Iron-copper sulfide	Tetrataenite
Fe	64.0	62.9	46.5
Ni	n.d.*	0.35	53.1
Co	0.05	n.d.	0.24
Cu	0.14	1.02	0.29
S	<u>36.7</u>	<u>36.2</u>	<u>0.05</u>
Totals	100.89	100.47	100.18
Atoms			
Fe	0.998	0.989	
Ni	—	0.005	
Co	—	—	
Cu	0.004	0.015	
S	<u>0.998</u>	<u>0.991</u>	
Totals	2.000	2.000	

*n.d. = not detected

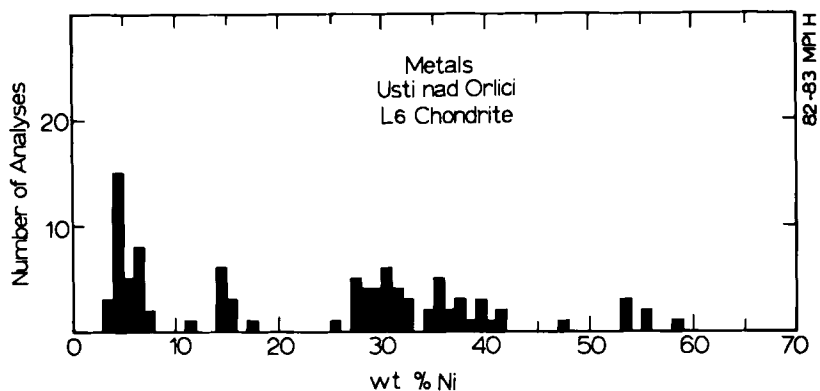
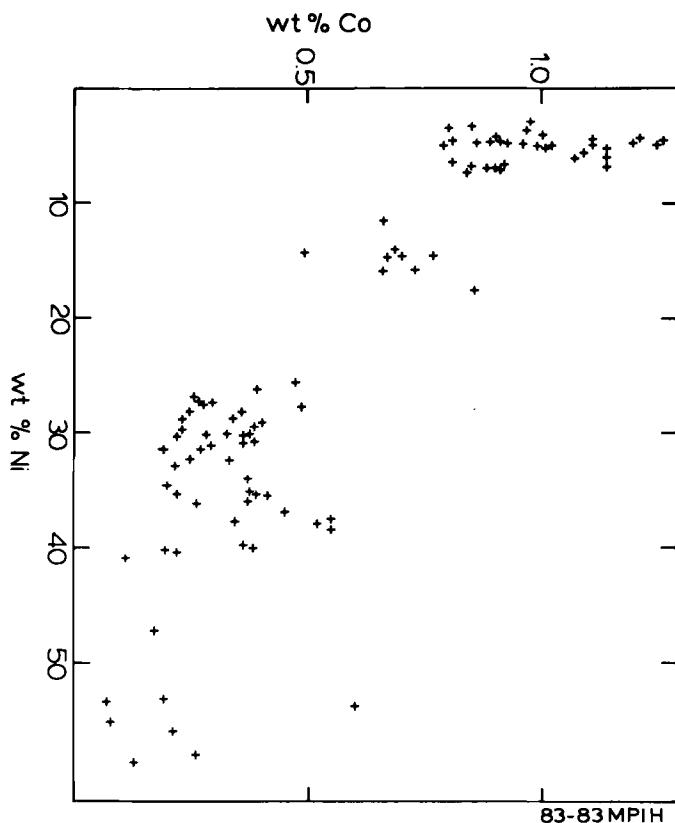


Fig. 15 Histogram with compositions of kamacite and taenite in Ustí nad Orlicí.



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Fig. 16 Ni versus Co relationship of metals in Ustí nad Orlicí. Note the high Co-content of kamacite.

display substitutional trends with lower slope than small chromites. This indicates that the substitutional trends of these elements may be dependent on the TiO_2 content of the chromite, or resulted from different equilibration behaviors with the neighboring silicates due to grain size effect. Selective oxidation of small chromites during metamorphism is very unlikely. The features observed, however, could have resulted from changing of f_{O_2} during the formation of the meteorite prior to thermal metamorphism. This would require initial high oxidizing conditions with decreasing f_{O_2} in the last stage during the formation of large chromite + metal + troilite.

Pentlandite, cubanite, and mackinawite bearing assemblages show that equilibration was active down to 200 °C.

REFERENCES

- Haggerty, S.E.**, 1972. Lunar 16: An opaque mineral study and systematic examination of compositional variations of spinels from Mare Fecunditatis. *Earth Planet. Sci. Lett.* 13, 328-352.

- Mason, B.**, 1979. Meteorites. In Data of Geochemistry, sixth edition, ed. M. Fleischer, Geol. Survey Prof. Paper, 440-B-1.
- Misra, K.C. and M.E. Fleet**, 1973. The chemical compositions of synthetic and natural pentlandite assemblages. *Economic Geology* **68**, 518-539.
- Müller, O., P.A. Baedeker and J.T. Wasson**, 1971. Relationship between siderophilic-element content and oxidation state of ordinary chondrites. *Geochim. Cosmochim. Acta* **35**, 1121-1137.
- Norish, K. and J.T. Hutton**, 1968. An accurate X-ray spectrographic method for the analysis of a wide range of geological samples. *Geochim. Cosmochim. Acta* **33**, 431-453.
- Ramdohr, P.**, 1973. The opaque minerals in stony meteorites. Elsevier Publ. Comp., 1-245.
- Reid, C.G.R. and K. Fredriksson**, 1982. The Madiun, Indonesia, chondrite. *Meteoritics* **17**, 27-30.
- Tuček, K.**, 1963. Nový československý meteorit — chondrit Ústí nad Orlicí — ve sbírkách Národního muzea v Praze. Čas. Národního muzea, Odd. přírod., 230-233.
- Van Schmus, W.R. and J.A. Wood**, 1967. A chemical-petrologic classification for chondritic meteorites. *Geochim. Cosmochim. Acta* **31**, 747-765.
- Yabuki, H. and A. El Goresy**, 1984. Spinel and chromite compositions in L- and LL-chondrites. In preparation.

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