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ZONED Cr, Fe-SPINEL FROM THE LA PEROUSE LAYERED  
 GABBRO, FAIRWEATHER RANGE, ALASKA

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Zoned spinel of unusual composition and morphology has been found in massive pyrrhotite-chalcopyrite-pentlandite ore from the La Perouse layered gabbro intrusion in the Fairweather Range, southeastern Alaska. The spinel grains show continuous zoning from cores with up to 53 wt.% Cr<sub>2</sub>O<sub>3</sub> to rims with less than 11 wt.% Cr<sub>2</sub>O<sub>3</sub>. Their composition is exceptional because they contain less than 0.32 wt.% MgO and less than 0.10 wt.% Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>. Also notable are the concentrations of MnO and V<sub>2</sub>O<sub>3</sub>, which reach 4.73 and 4.50 wt.%, respectively, in the cores. The spinel is thought to have crystallized at low oxygen fugacity and at temperatures above 900°C, directly from a sulfide melt that separated by immiscibility from the gabbroic parental magma.

## 1. Introduction

The Crillon–La Perouse intrusive body is a layered gabbro located in the southern Fairweather Range, southeastern Alaska. As mapped by Rossman [1] the body is roughly elliptical in plan, with dish-shaped layers lying between steep walls. The body underlies an area of approximately 375 km<sup>2</sup>, and has an exposed stratigraphic thickness of approximately 10,000 m. The exposed part of the intrusion consists dominantly of olivine gabbro, gabbro, and noritic gabbro. Ultramafic rocks, interlayered with olivine gabbro, are known to occur only in the vicinity of two nunataks in the Brady Glacier, about 5 km southeast of the main outcropping of the intrusion. Layering and textural characteristics indicate that the intrusion originated by cumulus processes. Preliminary data suggest that the intrusion has undergone only limited chemical dif-

ferentiation, as in the Axelgold layered gabbro in British Columbia [2].

Marginally economic concentrations of Ni-Cu ore have been established by diamond drilling in the vicinity of the Brady Glacier nunataks. Mineralization is predominantly in the form of disseminated sulfide, but several massive sulfide pods are exposed in one of the nunataks, and massive sulfide lenses are common in the drill core. Predominant sulfide phases are pyrrhotite, pentlandite, and chalcopyrite.

Detailed studies of the silicate and sulfide mineralogy and petrology of the intrusive body are in progress. These studies have revealed few atypical features insofar as the dominant rock- and ore-forming phases are concerned, but two findings are unusual: (1) neither the silicate rocks nor the sulfide lenses contain primary magnetite; and (2) graphite, occasionally as nearly pure seams over 0.3 m thick, is found in most of the

drill holes. (Lesser amounts of graphite have been noted throughout the exposed portion of the intrusion.)

During examination of a polished section of massive sulfide ore from one of the drill holes (NUC-10), a sparse, gray phase was noted that occurred principally as elongate grains with rounded ends (Fig. 1A and B). The specimen is from a massive sulfide zone, 2 ft thick, that occurs in poikilitic olivine gabbro, 176 m above the basal contact with biotite schist.

A concentrate of the unknown phase was obtained

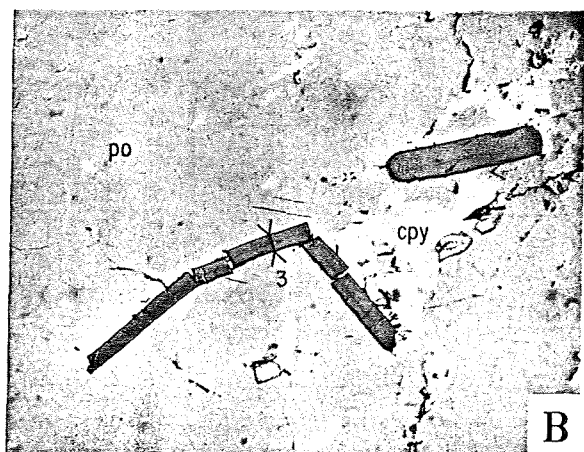
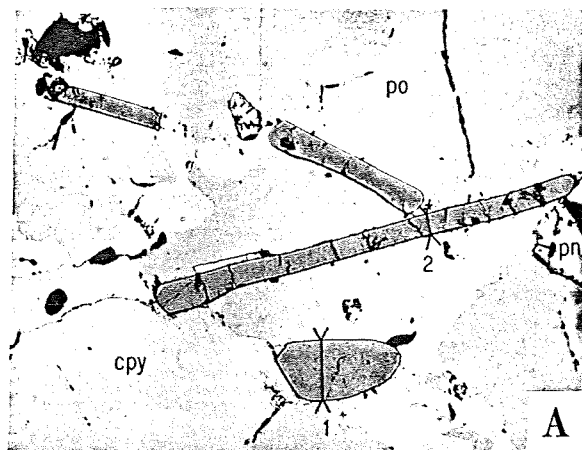


Fig. 1. Zoned spinel grains in massive sulfide host. Darker sulfide phase is pyrrhotite (po); dominant lighter phase, chalcopyrite (cpy). Smaller light areas with violarite alteration rims are pentlandite (pn). Numbers near marked traverses have been applied to individual grains to correlate with Table 1 and Fig. 2. Dimensions of each field are 0.70 mm  $\times$  0.89 mm.

by attacking an aliquot of coarsely ground, massive sulfide with a  $\text{Br}_2\text{-HCl}$  solution [4]. X-ray powder diffraction shows that the phase is a spinel with a cell edge between that of magnetite and chromite. Compositional zoning is reflected by incipient peak splitting. The spinel is strongly magnetic. Among the grains of the concentrate are found all gradations from rounded, chunky grains with minor development of octahedral faces to platelets with rounded edges that have been shown to be crystals flattened on {111}. Around their periphery the platelets may show development of crystal faces. Both morphological types are represented in Fig. 1A. The platelets appear as rods because they lie parallel to a weak foliation in the massive sulfide. Among the several hundred grains of the concentrate was a single, well-formed, twinned octahedron with octahedral edges about 0.5 mm long.

Analysis by electron microprobe has shown that the Cr,Fe-spinel has unusual composition and zoning. As this report was in review, a similar occurrence of spinel was reported from Kambalda Ni-sulfide deposit in Western Australia by Ewers et al. [3]. Previously, spinels of similarly low Al, Mg, and Ti content had been found only in a few meteorites.

## 2. Chemistry

### 2.1. Analytical procedures

Analyses were obtained with an ARL EMX-SM electron microprobe, using an accelerating potential of 15 kV and a sample current of 0.02 A on benitoite. Pure synthetic  $\text{Cr}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , MgO,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , NiO,  $\text{Mn}_2\text{O}_3$ , ZnO, and V were used as standards.  $K_\alpha$  lines were analyzed for all elements using an RAP crystal for Mg and Al and a LiF crystal for the other elements. Off-peak backgrounds were obtained at settings above and below peak settings for all elements except Cr and Fe. Matrix corrections were made by the theoretical scheme FRAME, developed by the National Bureau of Standards [5]. The data of Table 1 suggest that a deficiency in the correction scheme produces high sums for compositions characterized by high Cr content.

Data in Table 1, which represent compositional extremes of several spinel grains, are based on 5–10 points of analysis within each compositional zone. The

compositional profiles of Fig. 2 are based on single analyses at each point on the traverse.

## 2.2. Results

As seen in Table 1 and Fig. 2, the spinel grains are strongly zoned with respect to Cr, Fe, Mn and V. There is no evidence of a compositional gap, as found in some mantled spinels. These spinels are poorer in  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ , and  $\text{TiO}_2$  than any other terrestrial, Cr-

bearing spinels except those described by Ewers et al. [3]. Concentrations of  $\text{MnO}$  and  $\text{V}_2\text{O}_3$  are unusually high, particularly in the Cr-rich cores.

## 2.3. Comparisons

The unusual compositions of the spinels warrant comparison with spinels from other types of occurrence. (The comparison is valid also for the spinels reported by Ewers et al. [3].)

TABLE 1  
Compositional extremes and cations/unit cell for zoned spinel grains

	Grain 1		Grain 2		Grain 3	
	Cr-core	Fe-rim	Cr-core	Fe-rim	Cr-core	Fe-rim
$\text{Cr}_2\text{O}_3$	53.0	10.8	52.1	12.6	44.3	11.9
$\text{V}_2\text{O}_3$	4.50	1.17	3.25	1.25	1.46	1.39
$\text{Fe}_2\text{O}_3^*$	12.1	56.9	14.2	55.3	23.1	55.0
$\text{TiO}_2$	0.07	0.03	0.04	0.05	0.01	0.02
$\text{Al}_2\text{O}_3$	0.05	0.00	0.00	0.00	0.02	0.00
$\text{FeO}^*$	29.3	29.5	28.8	29.3	26.5	28.7
$\text{MnO}$	2.17	1.32	2.83	1.58	4.73	1.84
$\text{MgO}$	0.32	0.17	0.28	0.17	0.30	0.13
$\text{NiO}$	0.26	0.10	0.06	0.21	0.17	0.19
$\text{ZnO}$	0.34	0.00	0.32	0.00	0.00	0.00
Sum	102.11	99.99	101.88	100.46	100.59	99.17
<i>Cations/unit cell</i>						
	<i>Trivalent</i>					
Cr	12.27	2.61	12.10	3.03	10.46	2.90
V	1.06	0.28	0.77	0.31	0.35	0.34
Fe	2.67	13.10	3.14	12.66	5.19	12.76
Sum	16.00	15.99	16.01	16.00	16.00	16.00
	<i>Divalent</i>					
Fe	7.19	7.56	7.09	7.47	6.63	7.41
Mn	0.54	0.34	0.70	0.41	1.20	0.48
Mg	0.14	0.08	0.12	0.08	0.13	0.06
Ni	0.06	0.03	0.02	0.05	0.04	0.05
Zn	0.07	0.00	0.07	0.00	0.00	0.00
Sum	8.00	8.01	8.00	8.01	8.00	8.00
$100 \times \text{Fe}_2\text{O}_3^{**}$	17.9	83.4	20.6	80.7	33.2	81.5
$\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3$						

\* Values adjusted to  $\text{Fe}^{3+}/\text{Fe}^{2+}$  required by spinel stoichiometry.

\*\* Molecular ratio.

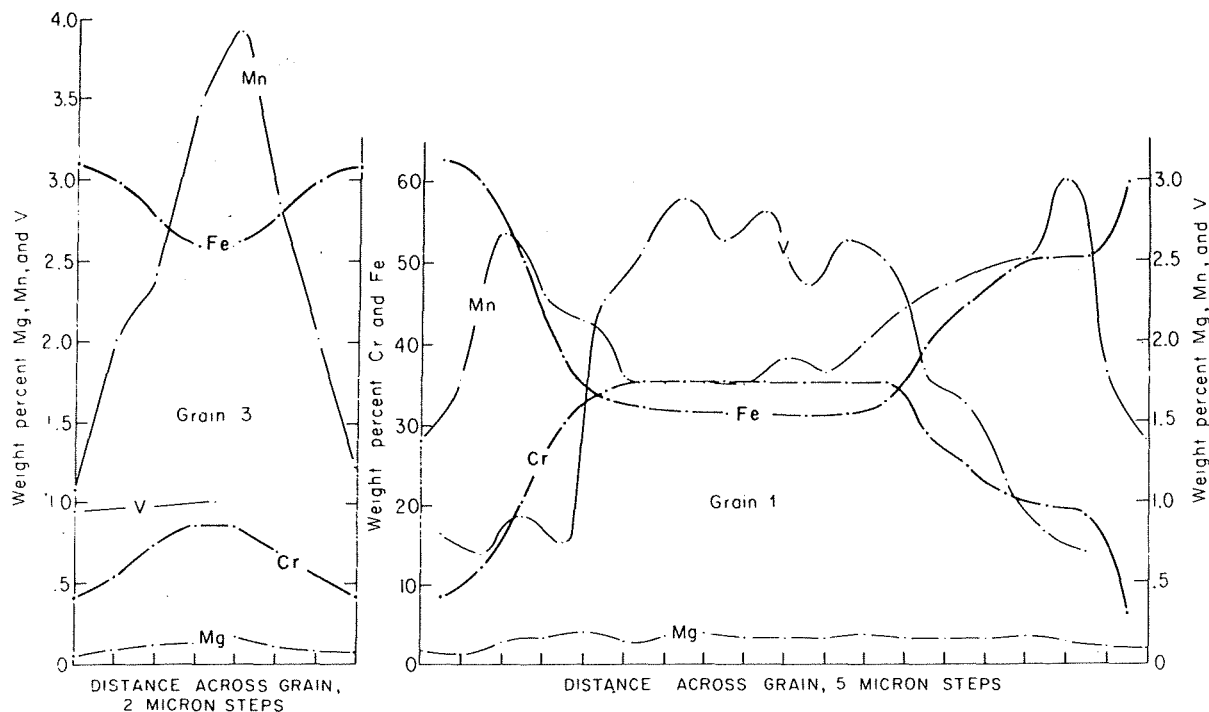


Fig. 2. Compositional profiles across two spinel grains (see Fig. 1A and B). Each dot represents a data point. Note the use of differing scales for distance and for Cr and Fe vs. Mg, Mn, and V.

Stevens [6] and Irvine [7] present data that characterize chromites associated with terrestrial, silicate magmas. In Cr content the cores of the La Perouse spinel grains are typical of chromites associated with stratiform mafic complexes or alpine-type peridotites. However, in Irvine's compilation, the highest ratio of  $\text{Cr}/(\text{Cr} + \text{Al})$  is 0.85 and the lowest  $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$  is 0.12; for the La Perouse Cr-rich cores the corresponding ratios are 1.00 and 0.02, respectively (Fig. 3). Another feature of their peculiar chemistry is the fact that the Cr-rich cores contain substantial percentages of  $\text{Fe}^{3+}$ . Irvine [7] has noted that chromites characterized by high  $\text{Fe}^{3+}/(\text{Cr} + \text{Al} + \text{Fe}^{3+})$  do not necessarily form under conditions of high  $f_{\text{O}_2}$ , as one might assume, and, coincidentally, are typical of southeastern Alaska.

Discussions of the chemistry of spinels in ultramafic nodules are found in Basu and MacGregor [8] and Smith and Dawson [9]; Haggerty [10] has studied spinels in kimberlite. Basu and MacGregor discuss five textural types of spinel, none similar to that we de-

scribe; Haggerty finds common examples of mantled and zoned spinels in kimberlite, but they deviate from the terrestrial norm in being richer in  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ .

Analysis of chromite inclusions in diamonds are presented by Meyer and Boyd [11] and Prinz et al. [12]. These chromites contain 10–16 wt.%  $\text{MgO}$  and 5–6 wt.%  $\text{Al}_2\text{O}_3$  and are richer in Cr (61–67 wt.%  $\text{Cr}_2\text{O}_3$ ) than any other terrestrial spinels. Meyer and Boyd present analyses for two unusual chromites from a single Sierra Leone diamond. The analyses are similar and average (wt.%):  $\text{Cr}_2\text{O}_3$  61.4;  $\text{FeO}$  31.3;  $\text{Al}_2\text{O}_3$  3.26;  $\text{MgO}$  0.52;  $\text{MnO}$  0.43;  $\text{ZnO}$  2.49; and  $\text{TiO}_2$  0.09. These are the closest terrestrial analogues to the spinels found by us and Ewers et al. [3].

Intensive studies of lunar mineralogy have provided a wealth of data for lunar spinels (e.g. Haggerty and Meyer [13] and Haggerty [14–16]). Unusual compositional trends and discontinuities have been defined, and many examples of compositional zoning and subsolidus reduction have been documented. Gradational overgrowths are interpreted to reflect continuous reac-

tion with liquid during slow crystallization [13]. Many lunar spinels are compositionally distinct from most terrestrial and meteoritic analogues by virtue of high concentrations of  $\text{TiO}_2$ . In this respect, as well as in  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  content, lunar spinels bear no resemblance to the La Perouse spinels.

Considerable attention has been devoted to the geochemistry of Cr in meteorites [17–20]. Although typical meteoritic spinels contain more  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ , and  $\text{TiO}_2$  than the Cr-rich cores of the La Perouse spinel grains, it is among meteoritic spinels that we finally find some of the chemical peculiarities of the La Perouse and Western Australian spinels. Two meteorites, Putnam and Bagdad, contain chromite with less than 0.11 wt.% of  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ , and  $\text{TiO}_2$ . It is significant that they are the only iron meteorites studied by Bunch and Keil in which the chromite is dispersed in the metal phase. The chondrites Bremervörde (Group H3), Bishunpur (H6), Khohar (H6), Krymka (L3), and Ngawi (LL3) contain chromite with less than 1 wt.% of  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ , and  $\text{TiO}_2$  [18]. Meteoritic chromites also typically contain up to 0.8 wt.%  $\text{V}_2\text{O}_3$  and some contain up to 4.2 wt.% MnO. Some chromites in iron meteorites with silicate inclusions contain more  $\text{Cr}_2\text{O}_3$  (70–75 wt.%) than any other known spinels.

Consideration of vanadium balance in chondrites by Bunch et al. [18] shows that V is enriched by a factor of 70 in chromite as compared with the bulk chondrite. Bunch and Olsen [17] note that the most reduced meteorites have the lowest  $\text{FeO}/(\text{FeO} + \text{MgO})$  and the most oxidized types the highest  $\text{FeO}/(\text{FeO} + \text{MgO})$ . (As noted below, although the La Perouse spinels must have formed at low  $f_{\text{O}_2}$ , they have a high  $\text{FeO}/(\text{FeO} + \text{MgO})$ , reflecting the extremely low Mg content of the sulfide melt.)

The preceding discussion has focused on comparison of the Cr-rich cores of the spinel grains (in essence chromite) with data from a voluminous literature on chromite compositions and shows that no truly comparable chromites have been known. Equally unusual are the zoning of the grains and the composition of their Fe-rich rims. We know of no Cr-bearing spinels comparable in composition to the rims, which might best be called chromian magnetites.

The paper by Ewers et al. [3] on the Kambalda ores mentions composite chromite-magnetite grains from a similar geologic setting, but unfortunately no information is given in the composition of the Cr-poor

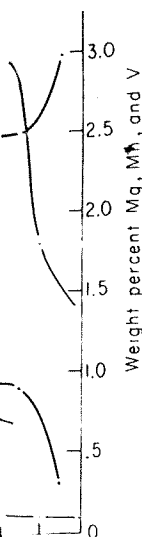
rims of their spinel grains or on the chemistry of the zoning. Their single analysis of a Kambalda Cr-rich core shows it to be richer in Al and Zn and poorer in Mn and V than the spinels from La Perouse.

### 3. Origin

It is well established that the composition of chromite is very sensitive to the conditions under which it forms [7,21]. That the La Perouse chromian spinels also display a unique morphology in an unusual host affords a further clue to their origin. As shown in Fig. 1A and B the grains occur in massive sulfide composed predominantly of pyrrhotite and chalcopyrite. The broken grain of Fig. 1B apparently formed early in the solidification history of the immiscible sulfide melt. No example of similar morphology for a natural spinel is known to us (see, for example, Ramdohr [22,23]). The closest morphological analogue known to us comes from crystallization of wüstite during quenching of experimental oxide-sulfide liquids [24].

We conclude that the La Perouse spinels owe their chemistry and unique morphology to crystallization from a sulfide melt that had segregated by immiscibility from gabbroic magma, and find it puzzling that such spinels have not been described previously. The recent report by Ewers et al. [3], while appearing sooner than we might have wished, lends substantial support to this theory. In addition to describing briefly a similar spinel occurrence, Ewers et al. conducted an experiment in which they introduced synthetic chromite into an Fe-Ni-Cu sulfide melt. They produced chromite grains rimmed by chromian magnetite and detected several tenths of a weight percent of Cr in the solidified sulfide melt.

A puzzling contrast is that the La Perouse spinel grains typically show only a suggestion of octahedral habit, whereas both the natural Kambalda chromite and the synthetic chromite grains described by Ewers et al. are euhedral to subhedral, with typical chromite morphology. No satisfying explanation for the rounded and tabular morphologies has occurred to us. Anhedral morphology is characteristic of some crystals that have grown rapidly, e.g., the wüstites of MacLean [24], but such quench crystals are more typically acicular. Moreover, rapid growth is difficult to envision considering that the grains grew from a system poor in Cr.



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As noted by Ewers et al., spinels thought to have crystallized from a sulfide melt are chemically distinct from spinels in the ultramafic rocks that host the massive sulfide bodies. For the La Perouse occurrence this contrast is strikingly shown in Fig. 3, a plot of  $\text{Cr}/(\text{Cr} + \text{Al})$  vs.  $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ . Additional strong contrasts are found in  $\text{MnO}$ ,  $\text{TiO}_2$ , and  $\text{V}_2\text{O}_5$  content. Chromites in the host rocks contain 0.07–0.41 wt.%  $\text{MnO}$  (average 0.29), 0.16–1.40 wt.%  $\text{V}_2\text{O}_5$  (average 0.79), and 0.07–1.0 wt.%  $\text{TiO}_2$  (average 0.45). Because

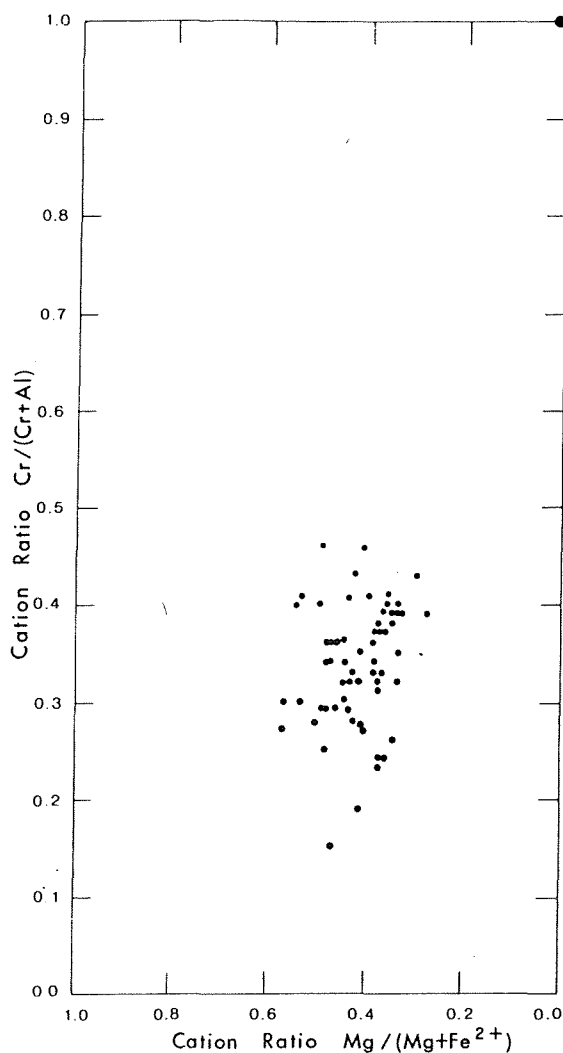


Fig. 3. Atomic  $\text{Cr}/(\text{Cr} + \text{Al})$  vs.  $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$  of the average Cr-rich core (large dot) and of 61 chromites from the ultramafic rocks of the nunatak area (small dots).

the only known chromites with comparably low concentrations of Al, Mg, and Ti are found dispersed in the metal phase of the meteorites Putnam and Bagdad [20], it would appear that Al- and Mg-poor chromites cannot crystallize from a natural silicate melt.

From a petrogenetic viewpoint, two important questions are: (1) whether extraordinary conditions are required to produce chromite from sulfide melts; and (2) what those conditions might be. Our prejudice is that such chromite may be quite common, and it is interesting that at least two additional occurrences are now reported from Australia [3]. Yet, despite years of intensive study of massive sulfide ores associated with mafic and ultramafic rocks, no such chromites have been noted heretofore. An important factor may be the relatively recent application of the electron microprobe. From a geochemical and thermodynamic point of view there seems to be no reason why chromite should not commonly crystallize from such sulfide melts. Because of its focus, the only known study of the Cr-Fe-S-O system [25] is not as informative as Naldrett's [26] study of the system Fe-S-O. Naldrett has shown that all sulfide melts will contain some oxygen that may or may not be fixed as an oxide phase depending on the crystallization history of the melt. Haggerty [14] showed that chromite is stable over a wide range of  $f_{\text{O}_2}$ - $T$  conditions in the system Fe-Cr-O, and that at 1000°C  $\text{FeCr}_2\text{O}_4$  is stable at  $f_{\text{O}_2}$  values more than 4 log units lower than wüstite (FeO).

El Goresy and Kullerud [27] found that above 700°C there is complete solid solution between  $\text{Fe}_{1-x}\text{S}$  and  $\text{Cr}_{1-x}\text{S}$ , an indication that there should be no difficulty in dissolving Cr in an Fe-bearing sulfide melt. (Dahl and Van Vlack [25] and Ewers et al. [3] also show that appreciable Cr will dissolve in a sulfide melt.) The situation in meteorites, where Cr- and Fe,Cr-sulfides are relatively common is rather the opposite of that we discuss. In iron meteorites, sulfur is a minor constituent, and troilite (FeS) and daubréelite ( $\text{FeCr}_2\text{S}_4$ ) are found in sulfide nodules. In a sulfide melt, oxygen is a minor component and, on crystallization, Cr, Mn, and V are partitioned preferentially into the oxide phase. Although all three of these elements form sulfides, nature and molecular orbital theory show that they all prefer oxide structures. Burns [28] notes that those transition metals which dominate sulfide mineralogy are those which form multiple  $\pi$

bonds with acceptor ligands such as sulfur. Formation of  $\pi$  bonds is increased when electrons fill the  $t_{2g}$  orbitals; Cr, Mn, and V have several unfilled  $t_{2g}$  orbitals regardless of valence or spin state.

We have noted that the ultramafic rocks and massive sulfide lenses at La Perouse appear to be free of primary magnetite and that the system contains substantial amounts of graphite. The situation is reversed in most mafic and ultramafic intrusions and associated massive sulfide occurrences [26]. We suggest that low oxygen fugacity may be responsible for crystallization of chromite from a sulfide melt, because at normal oxygen fugacities the sulfide melt will contain several percent oxygen [26,24], and minor Cr and V in the melt will be incorporated in relatively abundant magnetite. At low oxygen fugacities magnetite is unstable, but Cr may combine with small amounts of oxygen in the melt to form minor amounts of Cr-rich spinel [13].

Irvine [21, fig. 11] has calculated theoretical  $f_{O_2}$  isobars for spinel solid solutions coexisting with olivine and orthopyroxene. Although the La Perouse spinels apparently did not coexist with silicates, Irvine's calculations suggest that the Cr-rich cores formed at very low  $f_{O_2}$  and the configuration of the isobars is such that the compositional zoning toward magnetite can take place with only a modest increase in  $f_{O_2}$ . Depletion of the melt in Cr will also cause relative Fe enrichment in the spinel.

Cremer [29] has shown that  $FeCr_2O_4$  and  $Fe_3O_4$  are completely miscible at temperatures above 900°C, and the work of Naldrett [26] strongly suggests that spinel crystallization would have taken place above this temperature. We feel that zoning in the La Perouse spinel grains originated during crystallization, as suggested by Haggerty [13] for zoned lunar spinels. On the other hand, Bliss and MacLean [30] and Ulmer [31] propose that metamorphic reaction has caused zoning in chromites contained in serpentinite. While we cannot prove that the zoning we document has not been caused by subsolidus reaction, three factors weigh against this process: (1) the La Perouse spinel grains are found in unmetamorphosed rocks; (2) it is difficult to envision how a reaction process could produce the observed zoning against a sulfide host when all the elements that are found in lower concentration in the rims prefer the spinel structure; and (3) the complexity of the Mn and V zoning in grain 3 (Fig. 2) seems difficult to produce by reaction.

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