

NEW INVESTIGATIONS OF "KNORRINGITE-UVAROVITE GARNET" AND "CR-ESKOLA PYROXENE" IN UREILITES LEW 88774 AND NWA 766. C.A. Goodrich^{1,2}, G.E. Harlow² and T. Mikouchi³,
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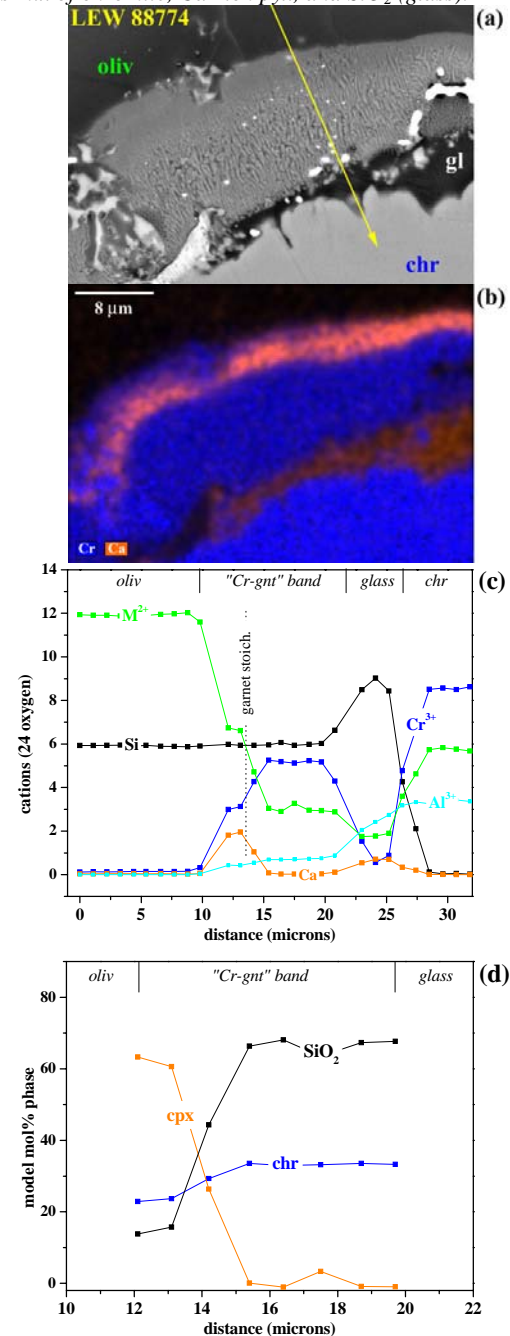
Introduction: LEW 88774 (LEW) and NWA 766 (NWA) are the only monomict ureilites that contain primary chromite [1-5]. Although both are at the ferroan extreme of the ureilite range (Fo 75-76), NWA is a typical olivine-pigeonite ureilite [5] interpreted to be a residue [6], while LEW is augite-bearing (olivine, augite and chromite enclosed in oikocrysts of exsolved opx) and interpreted to be a cumulate [6-8].

The chromites in LEW and NWA have ~5-40 μm -wide rims of Si,Al-rich glass (~70-77% SiO_2), with corroded edges against the glass. Within the glass, and/or partially embedded in the outer edges of the chromite grains, are a variety of Cr-rich minerals (Fe,Cr-carbides, Fe,Cr-sulfides, and eskolaite-corundum) thought to be products of late reduction [1-5]. In addition, [5,9] described two unusual, Cr-rich compositions that occur as discontinuous bands, ~5-20 μm wide, between the glass and surrounding olivine (both samples) or orthopyroxene (LEW only). These compositions were interpreted to be, respectively, knorringite-uvarovite garnet (albeit partially decomposed) and Cr-Eskola pyroxene formed as high-pressure phases during shock [5,9]. However, [10] suggested that the "garnet" was instead a metastable CrO-rich olivine. We report new SEM, EMPA, and EBSD observations of these "Cr-gnt" and "Cr-pyx" bands in LEW and NWA, and reconsider their origin.

New Observations: Our original observations of LEW, [9] showed the "Cr-gnt" bands to be homogeneous in their outer zones (near olivine) and the "Cr-pyx" bands to be completely homogeneous. Reexamination of this section with the JEOL 6390LV (KCC) and FE-Hitachi S-4700 (AMNH) SEM show that neither type of band is homogeneous at all (Fig. 1,2). Both consist of sub- μm scale symplectitic intergrowths of a high-Z phase and at least one lower-Z phase. The high-Z phase appears as ~radial lamellae in the outer zones, but assume more complex skeletal forms inward (Fig. 1a,2). The intergrowths coarsen inward in both types of band, but are finer overall in the "Cr-pyx" (Fig. 1a,2). In NWA, the structure of "Cr-gnt" bands is similar to that in LEW, but coarser.

Of our original (point) analyses of the "Cr-gnt" bands [9] only a few yielded stoichiometric garnet formulae; most showed widely varying excesses or deficiencies of trivalent cations. In contrast, all analyses of the "Cr-pyx" bands gave a consistent Cr-Eskola pyroxene composition.

Fig. 1. "Cr-Garnet" band. (a) BEI; (b) combined Cr and Ca x-ray maps; (c) compositional profile (location shown in [a]), recalculated as structural formula; (d) model of band as mix of chromite, Ca-rich pyx, and SiO_2 (glass).



We have now obtained additional data from x-ray maps and EDS and/or WDS profiles across ~20 areas of "Cr-gnt" or "Cr-pyx" in LEW and NWA. Results

show that all "Cr-gnt" bands have narrow subbands, defined by a sharp peak in Ca (Fig. 1), near their outer edges. A few analyses near the top of this peak yield garnet stoichiometry; outward from it they show deficiencies and inward they show excesses of trivalent cations (Fig. 1c). Nevertheless, across the entire band, Si/O is ~ 0.25 , appropriate for olivine or garnet. Some of the "Cr-pyx" bands (e.g. Fig. 3) also show, at their outer edges, Ca-peaks that yield a high-Ca pyx-like formula (with significant trivalent cations). Inward there is a sharp transition to the Cr-Eskola composition, which is relatively homogeneous across the rest of the band. Across the entire band, Si/O is ~ 0.333 , appropriate for pyroxene (Fig. 3). Olivine and opx adjacent to the bands have high Cr_2O_3 relative to "primary" compositions: ~ 1.0 - 1.4% (vs. 0.4%) in olivine and ~ 1.3 - 1.5% (vs. 1.0%) in opx.

We have modelled the analyses of both types of band as mixtures of chromite, high-Ca pyx, and Si-rich glass. Results suggest that the Ca-rich zones are dominated by pyx + chromite, and the inner zones by chromite + glass (Fig. 1d). This is consistent with the appearance of coarser-grained bands, in which the lower-Z phase in the Ca-rich zones is brighter (in BEI) than that in the inner zones.

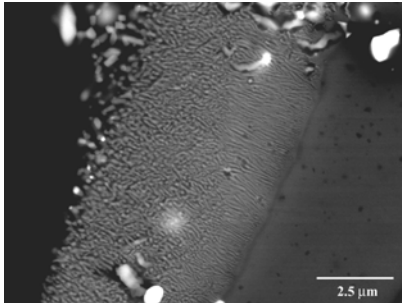


Fig. 2. BEI of "Cr-Pyx" band" in LEW,4.

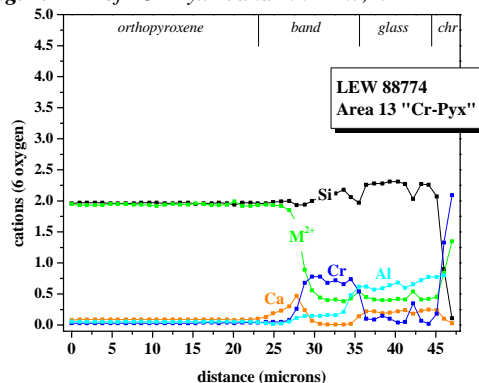


Fig. 3. Compositional profile across a "Cr-Pyx" band.

Electron Back Scattered Diffraction: We analyzed "Cr-gnt" and "Cr-pyx" in 5 areas of LEW,4 by EBSD (U. of Tokyo). Patterns obtained for the high-Z phase in coarse areas of the "Cr-gnt" can be indexed to the chromite structure, and indicate that all

lamellae have a common crystallographic orientation. No EBSD patterns were obtained for the low-Z phase in these areas, suggesting that they are glass. The Ca-rich outer zones of these bands, and all "Cr-pyx" bands, also failed to give EBSD patterns, probably due to their extremely fine grain size.

Discussion: The constancy of Si/O across each type of band suggests that they were once homogeneous phases that decomposed. Furthermore, the identity of Si/O (in each case) to that of the adjacent silicate suggests that they formed by 1) reaction of those silicates with Cr_2O_3 -enriched residual melt around the primary chromites [9], 2) a boundary reaction between silicate and chromite, or 3) reaction between silicate, chromite, and a Si-rich rim phase coating the chromite. Case 2 would require reduction of FeO, as the $\sum \text{M}^{2+}$ cations/24 oxygen in band + glass is less than that in adjacent silicate + chromite.

It is likely that the setting in which this occurred was one of impact excavation, and involved shock followed by rapid release of pressure, quenching, and reduction (by C). Thus, the Cr-rich bands may have formed as transient high-P phases that decomposed almost immediately. Our new data support the interpretation that the major part of the "Cr-pyx" bands was a Cr-Eskola pyroxene [9]. The reaction of opx with Cr-rich silicate melt probably proceeded as a front moving inward, and thus the Ca-rich outermost zones may represent the initial attempt by the pyroxene to accommodate excesses of Cr_2O_3 (by forming a cpx structure). Once Cr reached a critical level ($> \sim 10\%$), however, it was necessary to switch to a vacancy-bearing Cr-Eskola structure.

The formation of the "Cr-gnt" bands is less clear. We concur with [10] that most of this material is not consistent with garnet stoichiometry. However, it is unlikely that it was a CrO-rich olivine [10], because the Cr in the band is now clearly Cr^{3+} (as chromite), and conditions were not oxidizing. Possibly the Ca-rich outer zones formed, in the initial reaction, as a Cr_2O_3 -rich olivine (which decomposed to chromite+cpx:[11]). The majority of the interior of the bands has fairly constant stoichiometry approximating $\text{Mg}_{0.5}\text{CrSiO}_4$ (Fig. 1c). However, such a phase is unknown.

References: [1] Warren P.H. & Kallemeyn G.W. (1994) *LPSC* **25**, 1465. [2] Prinz M. et al. (1994) *LPSC* **25**, 1107. [3] Chikami J. et al. (1997) *MAPS* **32**, 343-348. [4] Goodrich C.A. (2001) *MAPS* **36**, A67. [5] Sikirdji M. & Warren P.H. (2001) *MAPS* **36**, A189. [6] Goodrich C.A. et al. (2004) *Chemie de Erde* **64**, 283-327. [7] Goodrich C.A. (1999) *MAPS* **34**, A44. [8] Goodrich C.A. & Keller L.P. (2000) *MAPS* **35**, A60. [9] Goodrich C.A. & Harlow G.E. (2001) *MAPS* **36**, A68. [10] Warren P.H. & Huber H. (2006) *LPSC* **37**, #2400. [11] Mosley D. (1984) *Am. Min.* **69**, 139-153.