

A SEARCH FOR SHOCKED CHROMITES IN FOSSIL METEORITES WITH RAMAN SPECTROSCOPY. S. S. Rout^{1,2*}, P. R. Heck^{1,2,3} and B. Schmitz^{1,4}, ¹Robert A. Pritzker Center for Meteoritics and Polar Studies, The Field Museum of Natural History, 1400 S. Lake Shore Drive, Chicago IL, 60605, USA. ²Chicago Center for Cosmochemistry, ³Department of Geophysical Sciences, The University of Chicago, 5734 S. Ellis Avenue, Chicago IL, 60637, USA. ⁴Department of Physics, Lund University, Lund, Sweden. *srout@fieldmuseum.org

Introduction: The L-chondrite parent body breakup (LCPB) in the asteroid belt ~470 Ma ago produced ejecta that was discovered as fossil meteorites (FM) in Sweden and abundant fossil micrometeorites worldwide within post LCPB mid-Ordovician sediments [1,2]. Both elemental and isotopic studies of relict chromite and chrome-spinel from these extraterrestrial materials have confirmed that they are L chondritic except one which was classified as winonaite-like [2-4]. Many of the modern L chondrite meteorites show extensive shock metamorphism and presence of high pressure phases within shock melt veins (SMVs) [5]. Two high-pressure polymorphs of chromite were discovered in a SMV of the Suizhou L6 chondrite [6]. Experiments determined the higher-pressure phase, xieite (orthorhombic CaTi_2O_4 -type), that forms between 18-23 GPa and 1800–1950°C and the intermediate phase, CF-chromite (orthorhombic CaFe_2O_4 -type), forming above ~12.5 Gpa and 1700-1800°C [7].

We therefore expect that the chromites from SMVs within the FM could have been also transformed in the shock event that lead to the LCPB. Finding shock signatures can help us constrain the P,T history of the FM and the LCPB event. Here, we present results from a survey for high pressure phases of chromite within shocked modern L chondrites and in FM.

Samples and Methods: Polished thin sections (PTS) from Tenham (L6, S6; ME 2617; #4) and Catherwood (L6, S6; ME 3066; #2, and #3) from the Field Museum collection and Coorara (L6, S6; USNM 5591-1) from the Smithsonian National Museum of Natural History were searched for chromite within and near SMVs using BSE/EDS mapping with the Field Museum's Zeiss Evo 60 SEM equipped with an Oxford Aztec SDD EDS system (Fig. 1). Chromite grains from these L6 chondrites, and polished mounts from [3] with chromites from Mount Tazerzait (L5), Hessele (H5), and FM from the Thorsberg (Österplana) and the Gärde (Brunflo) quarries were then studied using a HORIBA LabRAM HR Evolution confocal Raman system at the NUANCE facility, Northwestern University. A 532 nm Ar^+ laser was focused to ~1 μm spot and spectra were accumulated for 120 sec. Raman spectra were obtained from 47 chromite grains from 12 FM found in 8 sedimentary beds, 4 from Mount Tazerzait, 1 from Hessele, 20 grains from Coorara, 39 from Catherwood, and 11 from Tenham.

Results: Some of the grains from FM are highly fractured (Fig. 1d), similar to matrix chromite grains found outside the SMVs in L6 chondrites (Fig.1a). We found four grains within SMVs of Tenham and Catherwood (Fig. 1c) that we identified as intergrowths of chromite and CF-chromite or xieite, from their Raman spectra: primary peaks at ~605 cm^{-1} and ~684 cm^{-1} (Fig. 2). Chromites outside the SMVs show a distinct primary peak between 686-688 cm^{-1} and two secondary peaks at ~600 cm^{-1} and 496-500 cm^{-1} (Fig. 2). Most of the chromites within SMVs have only a broad peak before a primary peak at 680-685 cm^{-1} (Fig. 2). Raman spectra of the chromites can be divided into three groups: I) spectra similar to matrix chromites from Tenham, Catherwood and Coorara (51% of analyzed FM chromites); II) spectra with a large and broad peak between 500-600 cm^{-1} before the primary peak at 685-689 cm^{-1} (30% of analyzed FM chromites). We only find three chromites with group II spectra in the SMVs of Coorara L6 chondrite and none in the matrix of any of the analyzed modern meteorites; III) spectra similar to chromites in SMVs from Tenham, Catherwood and Coorara (19% of analyzed FM chromites; Fig. 2); IV) spectra produced from an intergrowth of matrix chromite and CF-chromite or xieite (none of FM chromites; Fig. 2).

Discussion: Group I spectra of FM chromites indicate that these are matrix chromites. At present we cannot explain the broad peak between 500-600 cm^{-1} in group II spectra. Our current dataset on group II spectra in modern meteorites is limited to three grains in SMVs only and we cannot determine with confidence yet if the FM chromites with group II spectra are from SMVs or matrix. The chromites with group III spectra inside the SMVs occur as closed packed polycrystalline aggregates (Fig. 2) and still have the Raman peak at ~684 cm^{-1} , characteristic of the spinel structure of low-pressure chromite. Thus, the crystal structure has not changed from spinel-type to something else, and is neither CF-type chromite nor xieite. It is difficult to differentiate between CF-chromite and xieite by Raman spectroscopy [7]. However, the absence of the secondary Raman peaks which would be expected in the spinel structure is unexpected. This could be due to transformation to an intermediate state that is stable at lower P,T than CF-chromite and xieite. This interme-

diate state could be produced by a fragmentation of the original chromite grain during shock loading or back-

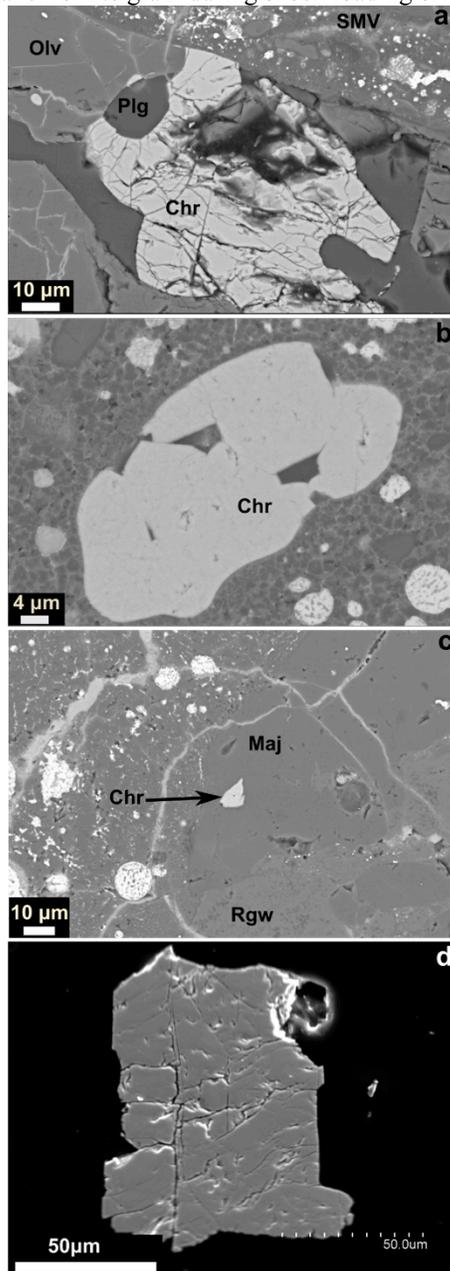


Fig. 1: Back Scattered Electron (BSE) images. (a) Matrix chromite (Chr) grain adjacent to a shock melt vein (SMV) in the Tenham. Oliv=Olivine, Plg=Plagioclase; (b) Chr inside a SMV in Catherwood. Bright areas are Fe-sulfide and Fe-metal. Dark line contrast within the grain most probably are grain boundaries separating the sub-grains. (c) Region inside a SMV in Catherwood. Chr grain (Catherwood_c4) is enclosed inside majorite (Maj), which is in contact with ringwoodite (Rgw) and fine grained matrix of the SMV. (d) Chromite grain from the fossil meteorite Sex 003.

transformed to a phase that is stable between normal, spinel-type chromite and higher pressure, CF-type chromite.

Conclusions: The majority of the FM chromite grains are matrix chromite (51%, Group I). None of the studied chromites from FM have been transformed all the way to the high-pressure phase CF-chromite or xieite but some grains (19%, Group III) do show signatures of intermediate shock similar to the chromite grains found within the SMVs of modern L chondrites. The remaining (30%, Group II) FM chromites could be from SMVs but this needs to be verified in follow up studies. TEM analysis of chromites from all groups from SMVs, matrix and FM will be done to investigate the shock effects in more detail.

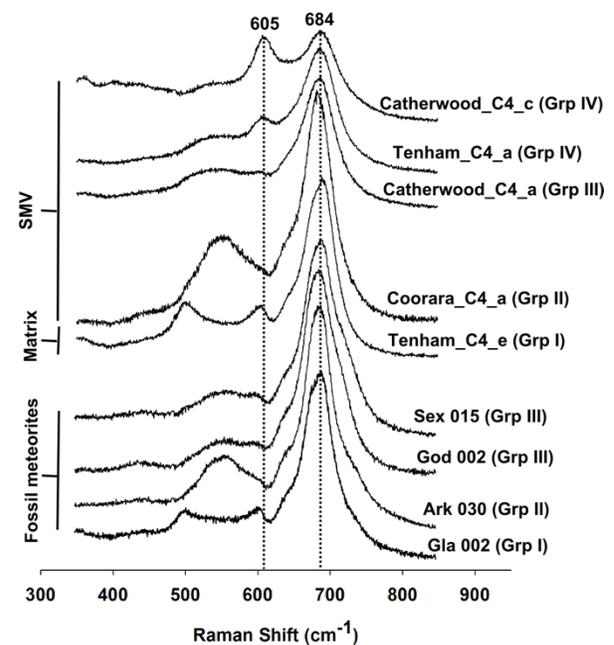


Fig. 2: Stacked Raman spectra of chromites from Tenham, Catherwood and Coorara L6 chondrites and fossil meteorites. The spectra from matrix chromites and chromites within SMVs of Tenham and Catherwood show the progressive transformation of low pressure chromite to high pressure chromite. The values on top indicate the peak position of Catherwood_C4 chromite (Fig. 1c).

References: [1] Schmitz B. et al. (2003) *Science* 300, 961–964. [2] Schmitz B. (2013) *Chemie der Erde* 73, 117-145. [3] Heck P. R. (2010) *Geochim. Cosmochim. Acta*, 74, 497–509. [4] Schmitz B. et al. (2014) *EPSL* 400, 145–152. [5] Sharp D. G. and DeCarli P. S. (2006) *Meteorite and Early Solar System II*, pp. 653–677. [6] Chen M. (2003) *Geochim. Cosmochim. Acta*, 67, 3937-3942. [7] Chen M. et al. (2003) *PNAS*, 100, 14651-14654.