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How to cite:

Bridges, John; Schofield, P. F.; Smith, A. D.; Scholl, A. and Grady, Monica (2002). Chemistry and valency spectra of Chromite in SNC meteorites. In: 33rd Lunar and Planetary Science Conference, 11-15 Mar 2002, Houston, Texas, USA.

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CHEMISTRY AND VALENCY SPECTRA OF CHROMITE IN SNC METEORITES: J. C. Bridges¹, P. F. Schofield¹, A. D. Smith², A. Scholl³ and M. M. Grady¹. ¹Dept. of Mineralogy, Natural History Museum, London SW7 5BD, UK. ²CLRC Daresbury Laboratory, Daresbury, WA4 4AD, UK. ³ALS, LBNL, Berkeley, CA, 94720, USA. j.bridges@nhm.ac.uk

Chromite as a petrogenetic indicator: Chromite ($\text{Fe}^{2+}\text{Mg}(\text{CrAlFe}^{3+})_2\text{O}_4 - (\text{MgFe}^{2+})_2\text{TiO}_4$) is one of the first few minerals to crystallize from basaltic or ultra-basic melts. This, together with its wide range of possible chemical compositions and $\text{Fe}^{3+}/\text{Fe}^{2+}$ variation, make it useful as a petrogenetic indicator. For instance, in terrestrial MORB the variation in $100\text{Cr}/(\text{Cr}+\text{Al})$ ratios of chromite has been related to partial melt extraction from the mantle (Fig. 1a), with higher ratios indicating derivation from a more depleted source region [1,2]. Variation in the $100\text{Mg}/(\text{Mg}+\text{Fe}^{2+})$ ratio or Fe^{3+} , Ti enrichment can be used to trace progressive fractional crystallisation. In this study we compare the composition of chromite in the SNC meteorites to that of terrestrial chromite in order to determine information about uncertain martian mantle Fe abundances [3], $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios, partial melting and fractional crystallisation.

Valence spectra: X-ray photoemission electron microscopy (XPEEM), which can provide spatial and quantitative information about valency in transition metals [4], has been carried out on some SNC chromite. XPEEM provides X-ray absorption spectra at the transition metal L-edges [5], in our case the Fe and Cr L-edges, whilst maintaining the spatial integrity of the data.

Chromite occurrence and composition: Chromite is present in the 3 lherzolitic shergottites and those basaltic shergottites DAG476, EETA79001A, SAU005 which contain olivine-orthopyroxene-chromite megacrysts [6]. It is also present in the ALH84001 orthopyroxenite and the Chassigny dunite.

Chromite analyses from SAU005, DAG476 and EETA79001(A) are plotted on Fig 1a,b,c together with terrestrial compositional fields. These meteorites have core compositions of $100\text{Cr}/(\text{Cr}+\text{Al})$ 74-87, $100\text{Mg}/(\text{Mg}+\text{Fe}^{2+})$ 12-36, $100\text{Fe}^{3+}/(\text{Fe}^{3+}+\text{Cr}+\text{Al})$ 0-5, $\text{TiO}_2 \leq 1$ wt%. Chromite in the lherzolitic shergottite ALHA77005 has a similar composition [6].

Several aspects of the shergottite chromite chemistry are apparent. There is no clear sign of fractional crystallisation of the parental melts e.g. the $100\text{Fe}^{3+}/(\text{Fe}^{3+}+\text{Cr}+\text{Al})$ ratios show little variation. There is limited variation in $100\text{Cr}/(\text{Cr}+\text{Al})$ ratios and so the parental melts to the primitive shergottite components were all derived from source regions which had undergone similar degrees of melt extraction. Fig. 1c shows the low $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios and Al contents of

martian, compared to terrestrial chromite from a wide range of lithologies.

The $100\text{Mg}/(\text{Mg}+\text{Fe}^{2+})$ ratios of the shergottite chromite. ALH84001 and Chassigny grains, do however suggest that sub-solidus equilibration between olivine, orthopyroxene and chromite took place – like in most cumulate igneous rocks. For instance, we measured the composition of olivine megacrysts in SAU005 as Fo62-72, and this is consistent with the $100\text{Mg}/(\text{Mg}+\text{Fe}^{2+})$ ratio of the chromite (16-22) equilibrating at $<1200^\circ\text{C}$, Fig. 1a [7]. Similarly, the composition of ALH84001 and Chassigny chromite varies along forsterite contours of the spinel prism, consistent with subsolidus equilibration.

ALH84001 and Chassigny chromite grain core compositions have $100\text{Cr}/(\text{Cr}+\text{Al})$ 77-83 and 73-89; $100\text{Mg}/(\text{Mg}+\text{Fe}^{2+})$ 6-21 and 12-19; $100\text{Fe}^{3+}/(\text{Fe}^{3+}+\text{Cr}+\text{Al})$ 4.5-10 and 4-10; and $\text{TiO}_2 \leq 2.7$ and 5.4 wt%. The higher $100\text{Fe}^{3+}/(\text{Fe}^{3+}+\text{Cr}+\text{Al})$ ratios and TiO_2 of these chromites compared to the primitive shergottitic components are consistent with the more fractionated nature of these cumulate rocks compared to the primitive shergottite components.

Mantle source compositions: The primitive, unfractionated composition of the shergottite chromite cores and lack of variation between the samples mean that they offer a chance to provide constraints on the composition of the mantle source. The martian mantle has generally been regarded as Fe-rich with FeO contents of 15-27 wt% compared to terrestrial values of 7.6-9 wt% [3, 8]. However, it has been suggested from the results of MELTS thermodynamic modelling [3] that the martian mantle has a terrestrial-like FeO content of 6.8 wt% and the shergottites were derived from 3% partial melting at 10 kbar. Our results are not consistent with this latter model. The $100\text{Mg}/(\text{Mg}+\text{Fe}^{2+})$ values of all the chromite plot at the lower end of the range of values for terrestrial basic and ultrabasic rocks and are distinct from MORB. The Al_2O_3 contents of the chromite are primarily a function of the low Al content of the martian mantle e.g. [8]. Similarly, although the $100\text{Mg}/(\text{Mg}+\text{Fe}^{2+})$ ratios of the SNC chromite have probably undergone subsolidus equilibration with olivine and orthopyroxene, the high FeO contents indicate mantle sources that are substantially more Fe-rich than the terrestrial mantle.

The mantle sources of the SNC chromite, in addition to being Fe-rich, seem to have had a rather homogenous degree of melt extraction. Despite the vary-

ing crystallisation ages of the shergottite samples (170-470 Ma Rb-Sr [9]) the limited variation in $100\text{Cr}/(\text{Cr}+\text{Al})$ suggests that their melts' source regions were uniformly Al-poor.

Fe³⁺/Fe²⁺ ratios of shergottite mantle sources.

The oxygen fugacity of the nakhlite's melt has been constrained using the composition of Fe-Ti oxides as around the QFM buffer [10]. The more fractionated shergottite melts which mixed with the primitive megacrysts assemblages in the basaltic shergottites studied here may crystallised under a variety of $f\text{O}_2$ between QFM and IW [11,12]. The $f\text{O}_2$ of the megacrysts and lherzolitic shergottites are not well established. On the basis of thermodynamic models and the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios of pyroxene in shergottites it has been suggested that they crystallised 1 to 4 \log_{10} units below QFM [3]. The low $100\text{Fe}^{3+}/(\text{Fe}^{3+}+\text{Cr}+\text{Al})$ ratios of determined here are consistent with such oxygen fugacities. Chromite with $100\text{Fe}^{3+}/(\text{Fe}^{3+}+\text{Cr}+\text{Al})$ ratios of <5 have been crystallised in experiments at 1300°C and $-\log f\text{O}_2$ of 8–12 [13].

XPEEM experiments: These were conducted at the Advanced Light Source in order to obtain valence-state images and L-edge X-ray Absorption Near Edge Structure (XANES) spectra were taken on selected areas of chromite grains within SAU005. These spectra (Fig. 2) can be used to monitor and quantify the variation in oxidation state of both Fe and the Cr across the chromite grains. This in turn will provide a time dependent image of the variation of the oxygen fugacity of the martian melt.

Conclusions: The composition and valency of chromites in primitive shergottite components are consistent with Al-poor, Fe-rich, low $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $f\text{O}_2$ 1 to 4 \log_{10} units below QFM, mantle source regions. These source regions - of diverse age and locality - had undergone an homogenous degree of melt extraction as shown by limited $100\text{Cr}/(\text{Cr}+\text{Al})$ variation between the different meteorites. In contrast, chromite in ALH84001 and Chassigny shows that their parental melts were more fractionated, with relatively enriched Ti and Fe^{3+} contents.

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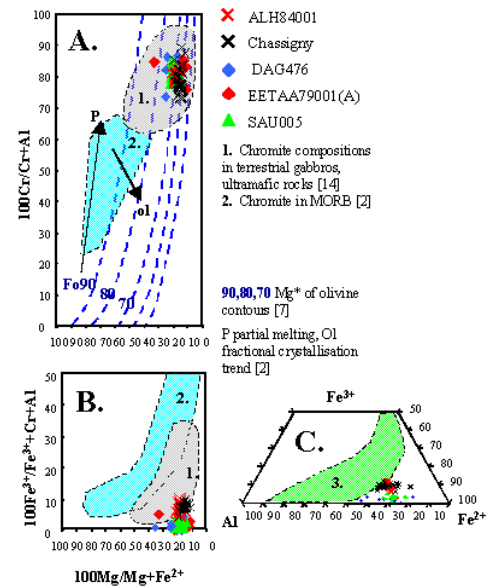


Figure 1a-c. Chromite atomic compositions in SNC meteorites. SNC chromite has high Fe, low $\text{Fe}^{3+}/\text{Fe}^{2+}$ and low Al contents compared to most terrestrial chromites. The limited variation in $100\text{Cr}/(\text{Cr}+\text{Al})$ ratios suggests that the source regions of the shergottites (DAG476, SAU005, EETA79001) experienced similar degrees of melt extraction. The spread of chromite compositions along contours of olivine composition [7] applicable to the SNC meteorites suggest that some subsolidus Fe/Mg equilibration between the silicate phases and chromite grains has taken place. Not shown on this figure is the separate fractionation of the chromite rims' compositions. Rims of chromite in the groundmass have $\text{TiO}_2 \leq 18$ wt% and high and low $100\text{Fe}^{3+}/(\text{Fe}^{3+}+\text{Cr}+\text{Al})$ ratios of either 14-20 or 1-4. This is due to exposure to fractionated melt [6,15]. EPMA analyses Cameca SX50 at 20 kV, 25 nA and JEOL 5400 ASEM.

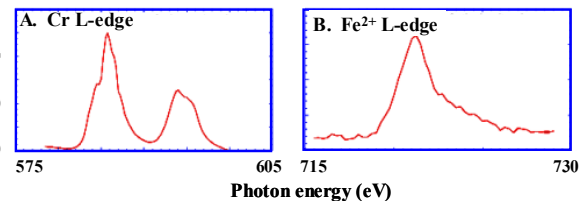


Figure 2a,b. L-edge XANES spectra from a $30 \mu\text{m}$ chromite grain of SAU005. The spectra indicate a predominance of Cr^{3+} (A) and Fe^{2+} (B) across the entire grain. The area selectivity provided by XPEEM allows individual L-edge XANES spectra to be taken from submicron areas across the entire grain. Vertical scale normalized intensity.