ESRF'	**Experiment title:** Site partitioning and oxidation state of chromium in spine1 from high temperature refractory ceramics: an X-ray absorption study.	**Experiment number:** HC-502
Beamline: D8/GILDA	**Date of experiment:** from: 22-05- 1996 to: 24-05- 1996	**Date of report:** 10-02-1997
Shifts: 6	**Local contact(s):** Stefano Colonna	*Received at ESRF:* 04 MAR. 1998

Names and affiliations of applicants (* indicates experimentalists):

Gilberto Artioli*, Dip. Scienze della Terra, Univ. Milano
Massimo Valle, ICRA
Simona Quartieri*, Dip. Scienze della Terra, Univ. Modena
Ganni Antonioli, Dip. Fisica, Universita di Parma
Davide Levy*, Dip. Scienze della Terra, Univ. Modena
Alessandro Gualtieri*, Dip. Scienze della Terra, Univ. Modena

Report:

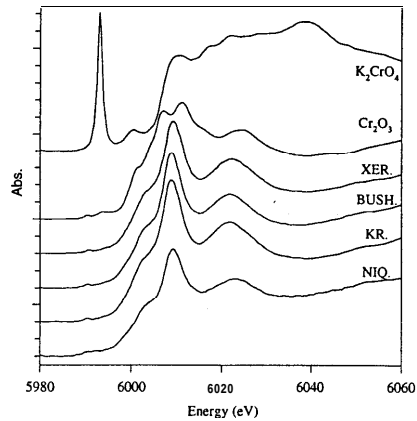
The crystal chemistry of Cr in synthetic and natural spinels was investigated by XAS spectroscopy on the Cr K edge. Cr_2O_3 and $K_2Cr_2O_4$ were used as valence and coordination standards: trivalent Cr in Cr_2O_3 is octahedrally coordinated, hexavalent Cr in $K_2Cr_2O_4$ is in tetrahedral coordination. Synthetic spinels were investigated because they are major phases in high temperature refractory ceramics and the crystal chemistry of Cr is crucial in determining the physical properties of the final product. Natural chromites, from Xerolivado (XER.), Bushveld (BUSH), Krasta (KR) and Niquelandia (NIQ), were studied for comparison.

All natural chromites and the synthetic Cr-rich spinels not associated with mullite unambiguously show the chromium cations to be trivalent and in octahedral coordination, independently of the synthesis procedures and temperature of formation.

A few spinel-mullite associations were also investigated (mullite 30 wt%-spine1 70 wt% and mullite 70 wt%-spine1 30 wt%; 3.5 wt% of Cr_2O_3 in the starting material). In the more spinel-rich sample the XANES spectrum is essentially equivalent to those observed in pure spinels and chrornite samples. In the sample where mullite is prevalent, the XANES spectrum has two additional features close to main edge peak. These features closely match those observed in the XANES spectrum of Cr_2O_3, and indicate the presence of trivalent

chromium in a distorted octahedral environment outside the spine1 structure. It is not clear whether these Cr ions are in the corundum-type structure (corundum-eskolaite solid solution) or in the HT mullite phase. More studies are planned to clarify the problem. In any case there is clear evidence of limited Cr solubility in the spine1 structure, possibly due to the inhibiting effect of mullite.

XANES Chromites



XANES synthetic Mullite and Spine1