

REDOX CONDITIONS FROM XAS SPECTROSCOPY ON BRACHINITES AND BRACHINITE-LIKE UNGROUPED ACHONDRITES. Cuppone¹ T., Lepore¹ G.O., Giuli² G., De Santis² V., Hole³ C., Carli C.⁴, Pratesi¹ G.. ¹Dipartimento di Scienze della Terra, Università degli Studi di Firenze, Firenze, Italy, ²Scuola di Scienze e Tecnologia – Sezione Geologia, Università di Camerino Camerino, Italy, ³European Synchrotron Radiation Facility, Grenoble, France, ⁴Istituto di Astrofisica e Planetologia Spaziali - INAF, Roma, Italy (tiberio.cuppone@unfi.it).

Introduction: Brachinites are olivine-rich primitive achondrites which record planetary differentiation onset on asteroidal bodies, displaying equilibrated textures and homogenous mineral phases with oxidised mineral chemistry (Fa₂₆₋₃₆, Fig. 1) [1]. Ungrouped brachinite-like achondrite meteorites (UBAs) share many similarities with brachinites [2], whose asteroidal counterpart, as well as for brachinites, has not been identified to date. Their close compositional and textural affinities, pose questions about the possible genetic link among these two meteorite groups, i.e. whether they derive from a single heterogeneous or more compositionally affine parent body(ies) [3]. Constraining the oxidation state of starting material could help to identify the chondritic parental body, but this information has been obtained only indirectly, through thermodynamic calculation, starting from mineral composition assemblage and equilibrium temperature between mineral phases [4]. Few works tried to directly constrain oxygen fugacities of brachinites source material, by measuring Cr valence in olivines of some brachinites and brachinite-like [5], while V valences in chromites from different meteorite groups, including brachinites, was investigated in [6]. Our purpose is to obtain a large and complete cation valence dataset on olivines, low/high-Ca pyroxenes and chromites from brachinites and brachinite-like achondrites by means of X-ray absorption spectroscopy (XAS), to directly constrain oxygen fugacity of source material and possibly better define both the genetic relationship between them and which kind of material formed the(ir) parental body(ies).

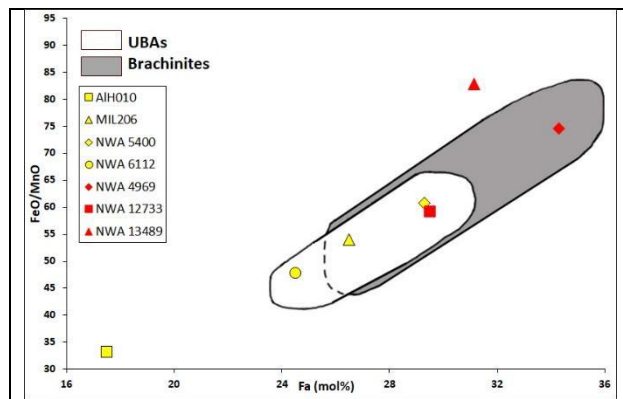


Fig 1 – Fa mol% versus FeO-MnO ratio for brachinite and UBA olivines studied.

Sample and analyses: A whole set of XAS measurements at V, Cr and Fe K-edges has been performed on 3 brachinites, NWA 4969, NWA 12733, NWA 13489 and 4 UBAs, AIH 010, MIL 090206, NWA 5400, NWA 6112 (Fig. 1).

Experimental methods: Micro-XAS measurements were carried out at ID21 beamline, ESRF, using Si(311) monochromator crystals. Beam spot on the sample surface was approximately 1000*500 nm². Spectra were measured in fluorescence mode using a silicon drift detector.

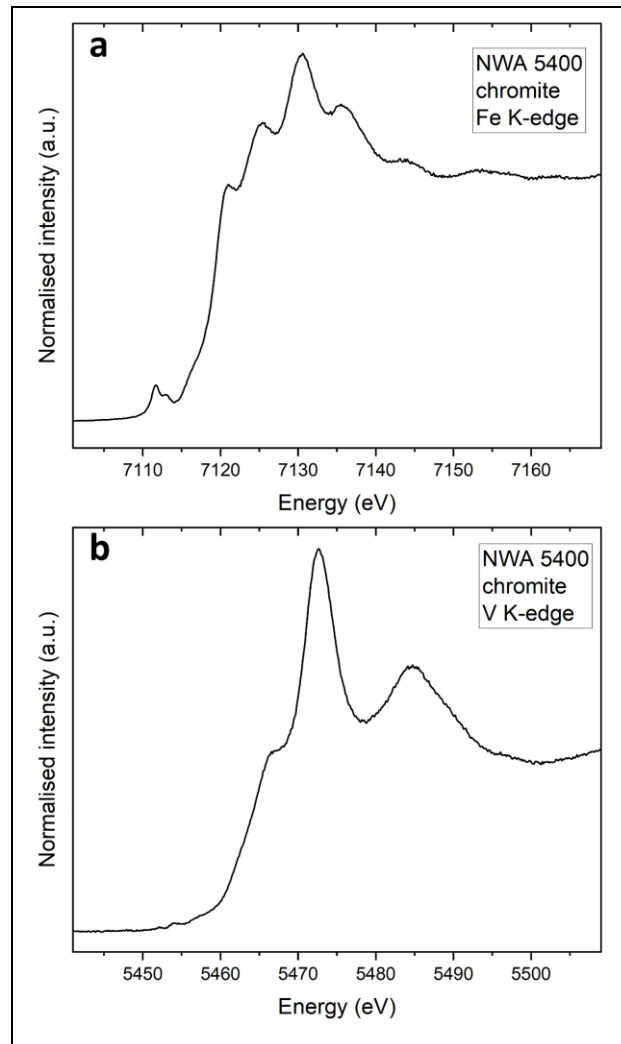


Fig 2 – Fe (a) and V (b) K-edge XANES region for sample NWA 5400

For each meteorite, we collected multiple spectra for each metal edge on several mineral grains after XRF elemental maps inspection (for minerals identification) of several meteorite areas.

Preliminary results: Preliminary results from XANES on chromite crystals from UBA sample NWA 5400 show that Fe is mainly present as Fe^{2+} in tetrahedral coordination while V is present as V^{2+} (Fig. 2). Quantitative EXAFS fit performed at V K-edge shows that divalent V is hosted in octahedra with a V-O distance of 2.00(1) Å and II and III shell distances (V-Cr=2.99(2) Å; V-Fe=3.49(2) Å in excellent agreement with V positioned at the 16d position.

Vanadium divalent state has been rarely described in natural samples [e.g. 7], thus indicating extremely reduced oxygen fugacity values for the NWA 5400 source material. We will expand XAS analysis to all meteorite dataset, comparing valence states of Fe, V and Cr in all the analysed mineral phases. Possibly, even analysing Ti K-edge in future analytical sessions.

References: [1] Keil K. (2014) *Chemie der Erde* 74, 311–329. [2] Day J.M.D. et al., (2012) *Nature Geosc.* 5, 614-617. [3] Cuppone et al., in publication [4] Gardner-Vandy K.G. et al., (2013) *Geochimica et Cosmochimica Acta* 122, 36-57. [5] Goodrich C.A. et al., (2014) *Geochimica et Cosmochimica Acta* 135, 126-169. [6] Righter K. et al. (2016) *American Mineralogist* 101, 1928-1942. [7] Camara et al. (2019) *Minerals* 9, 4.

Acknowledgements: This work is supported by the ASI-INAF agreement n.2018-16-HH.0, OI-BODIES project. We thank the Natural History Museum Bern and the National Institute for Polar Research for the meteorite samples (AIH010 and MIL 090206 respectively). We acknowledge the European Synchrotron Radiation Facility (ESRF) for provision of synchrotron radiation facilities (Exp. ES-1400) and we thank ID21 staff for the support during the measurements.