

Local structures of Ca, Ti and Fe in meteorite fusion crusts

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Abstract. The local structures of meteorite fusion crusts were studied by Ca, Ti and Fe K-edge XANES and EXAFS spectroscopy. The surface of meteorites were melted and volatilized with extreme high temperature and large temperature gradient when meteorites were rushed into atmosphere. This study indicated that meteorite fusion crusts have unique local structures. The local structures of fusion crusts differ from tektites especially in intensity of the shoulder in the rising flank of the edge in Ca XANES spectra. It is consistent with chemical composition change by the volatilization of Si at fusion during atmospheric entry. The high estimated $\text{Fe}^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$ ratio in meteorite fusion crusts indicates that meteorite fusion crusts are formed into atmospheric oxidation condition. The Ca-O distances in meteorite fusion crusts are 2.61-2.66 Å and are extremely longer than in other natural glasses. The fusion crusts have unique local structure since they experienced extremely high temperature and short quenching time. The XAFS method is effective in distinction of meteorite fusion crusts and classification of natural glass.

1. Introduction

All meteorites develop fusion crusts during atmospheric entry due to heating by hypervelocity collisions with air molecules [5]. Meteorite fusion crusts (fusion crusts) have been formed in extremely short times (several seconds) under the Earth's atmosphere conditions [2]. The surface of meteorites were melted and volatilized with extreme high temperature and large temperature gradient when meteorites were rushed into atmosphere. It is assumed that the unique local structures were formed in fusion crust glass under the ultra-high temperature with volatilization and rapid quenching process. Local structural difference can be predicted between fusion crusts and bulk. Local structures are affected by the pressure and temperature conditions during the glass formation and quenching process [7, 9, 16]. Wang et al. [9], Tobase et al. [11] and Wang et al. [13] reported unique Ti, Ca, Fe local structures in meteorite impact-related glasses and tektite. Upon a devastating impact of a giant meteoroid on the Earth, particles of the Earth's surface were melted and catapulted into outer space, where they finally solidified and fell back to the Earth as tektites. Tektites should be passed through several kinds of vitrification processes. Since local structures in glass are strongly related to forming process, comparing local structures of fusion crusts and impact-related glasses are important to reveal the vitrification processes of natural glasses. It is indicated that the XAFS method is useful for classification of natural glasses and distinction of meteorite fusion crusts.

2. Sample and Experiment

In order to study the local structures around Ca, Ti and Fe atoms in the fusion crusts of L5 chondrite (unnamed, North African), Dar al Gani 456 (L6 chondrite), millbillillie (Eucrite achondrite), Allende (CV3 carbonaceous chondrite) and Odessa (Iron meteorite, IAB) meteorites, we prepared several



reference materials such as minerals, tektite glasses, impact glasses and volcanic glasses. The Ca, Ti, and Fe K-edge XAFS measurements were performed at beam line BL-9C, equipped with Si (111) double-crystal monochromator, Cu calibration, fluorescence mode, lytle detector, of the Photon Factory, KEK, Tsukuba, Japan. The EXAFS functions were transformed into the radial distribution functions. In order to obtain information on the detailed structure parameters, we conducted parameter fitting with analytical EXAFS formulae. Analysis of XAFS data was performed by using XAFS93 and MBF93 programs [17].

3. Result and discussion

3.1 XANES spectra of Ca, Ti and Fe

The Ca, Ti and Fe XANES spectra are shown in figure 1 and 2. The Ca XANES spectra in fusion crusts are unique and have various pre-edge and shoulder intensity (figure 1A). The pre-edge peak observed in Dar al Gani 456 is the highest intensity. It indicates that site symmetry of Dar al Gani 456 is lower than other meteorites based on the relative intensity of the pre-edge [6]. The pre-edge intensity of L5 chondrite is the lowest and the local symmetry around Ca in L5 chondrite is higher than other fusion crusts. XANES pattern of Ca for tektite is unique and distinguishable from other reference materials such as volcanic glass (obsidian), impact glass (impactite) and mineral (apatite) [11]. All fusion crusts have almost similar spectra which differ from any other reference materials. Ca XANES in fusion crusts differ from tektites especially in shoulder intensity (figure 1B). The silicon contents of calcium aluminosilicate glass has positive correlation to the shoulder intensity [6]. Table 2 shows that chemical composition of fusion crusts and reference materials. Combining the result of silicate content and shoulder intensity, silicon content of fusion crusts also have positive correlation to shoulder intensity. Although the value of $\text{CaO}/\text{Al}_2\text{O}_3$ is lower than 1, the correlation ship of silicon content and shoulder intensity is consistent with that of Neuville et al., 2004 [6]. Lower silicon content of fusion crusts related to chemical composition change by the volatilization of Si at fusion during atmospheric entry. The XANES pattern of Ca indicates that the meteorite fusion crusts experienced high temperature with volatilization.

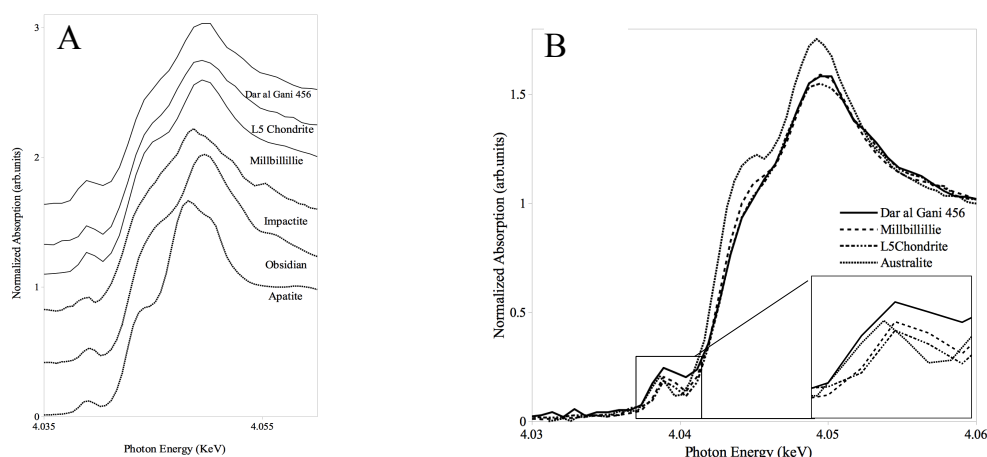


Figure 1. (A) Experimental Ca XANES spectra of meteorite fusion crusts and reference materials. (B) Detailed comparison of XANES spectra of Ca in Dar al Gani 456, L5chondrite, Millbillillie and australite tektite.

Comparing to previous study of Wang et al. [12], Ti XANES spectra of fusion crusts are similar to that of moldavite-green tektite (figure 2A). Shape of Ti XANES spectra of fusion crusts in Millbillillie and Allende are similar to moldavite-green. However XANES spectra of fusion crusts are slightly different to that of tektite. The pre-edge peak intensity is related to Ti coordination number. The pre-edge peak intensities of fusion crusts are 22.6-28.7% (the peak top of spectra is defined as 100%) and

are higher than that of moldavite-green tektite. The pre-edge peak intensity of fusion crusts indicates that fusion crusts have mixture of five- and six- coordinated Ti. Since coordination environment in Ti is related to formation temperature, it is presumed that forming temperature of fusion crusts is higher than that of moldavite-green tektite.

The Fe XANES spectra of fusion crusts (figure 2B) are different from tektites and impact glasses [14]. The local structures of Fe in fusion crusts have unique local structures. The threshold energy of Fe is strongly related to oxidation state of Fe ions. Since the threshold energy of moldavite-green tektite is lower than fusion crusts and impact glasses, the total charge of Fe ions in fusion crusts is higher than that in tektites. According to Wang et al. [14], the estimated $\text{Fe}^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$ ratio in fusion crusts are 0.34-0.66 and that in tektites are 0.04-0.13. The estimated $\text{Fe}^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$ ratio in fusion crusts are higher than that in tektite. Tektites are well known that they were produced in minimal oxidation environment such as space. The high estimated $\text{Fe}^{3+}/(\text{Fe}^{2+}+\text{Fe}^{3+})$ ratio in fusion crusts indicates that fusion crusts are formed into atmospheric oxidation condition. The threshold energy of fusion crusts have almost same as suevite impact glass because of meteorite fusion crusts formed in the atmosphere.

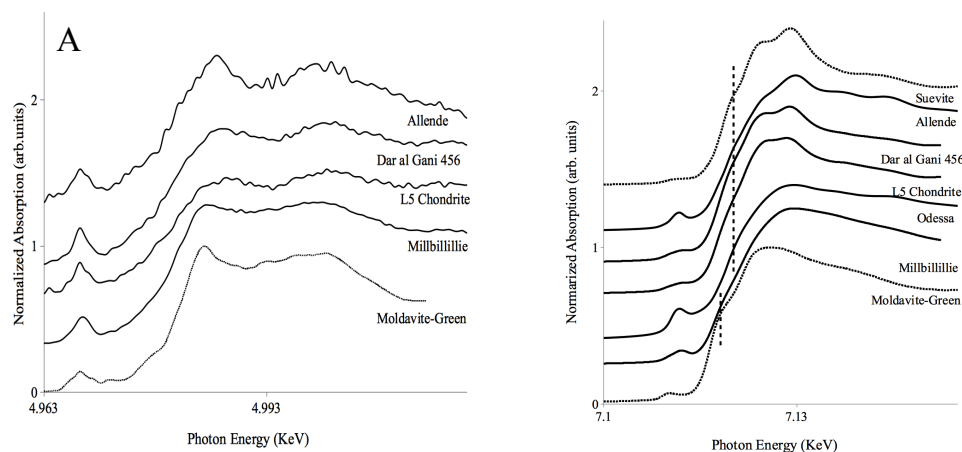


Figure 2. (A) Experimental Ti and (B) Fe spectra of meteorite fusion crusts and moldavite tektite. Solid lines are meteorite fusion crusts, dotted line is tektite and impact glass. Vertical dashed lines are threshold energy.

3.2 Radial distribution function and bonding distances of Ca, Ti and Fe

The EXAFS $k^3\chi(k)$ functions were transformed into the radial distribution functions (RDF) for the Ca, Ti and Fe k-edge of fusion crusts, as shown in figure 3. In order to obtain information on the detailed structures parameters, we conducted parameter fitting with analytical EXAFS formulae. The obtained structural parameters of Ca, Ti, Fe are summarized table 1.

The Ca-O distances in fusion crusts are 2.61-2.66 Å and are extremely longer than that in tektites (2.4-2.419 Å) and impact glasses (2.438 Å) [11]. The fusion crusts have unique local structures since they were experienced extremely high temperature and short quenching time. Ca-O distance of Allende is much longer than that of other fusion crusts. Longer Ca-O distance indicated that forming temperature of Allende fusion crusts is higher than that of other fusion crusts.

The Ti-O distances in fusion crusts are 1.90-2.00 Å and are shorter than that in moldavite-green tektite (2.001 Å). The estimated coordination number of Ti in meteorite fusion crusts are 5- and 6-coordinated Ti and are lower than that in moldavite-green tektite. Since coordination number of Ti has positive correlation to forming temperature, forming temperatures of fusion crusts are higher than that of moldavite-green tektite.

The Fe-O distances in fusion crusts are 2.02- 2.11 Å. The Fe-O distance in Odessa is the longest which is 2.11 Å. Wang et al. [14] reported Fe-O distances in tektites are 2.01-2.06 Å and Fe-O distance

in natural glasses are 1.99-2.11 Å. The pre-edge intensity has positive correlation to Fe-O distance. The estimated coordination number in fusion crusts are mixture of 5- and 6- coordinated Fe and are higher than that in tektites.

The local structures of cation in fusion crusts are unique and the XAFS method is effective in distinction of fusion crusts and classification of natural glasses.

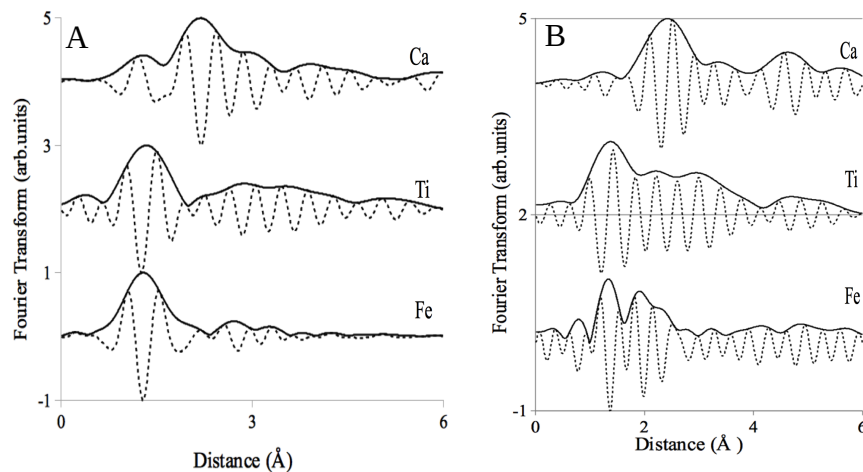


Figure 3. Fourier Transform of the Ca, Ti and Fe K-edge EXAFS oscillation function $k^3\chi(k)$ of Millbillillie (A) and L5 chondrite (B).

Table 1. The structural parameters determined by XAFS.

Sample	Ca-O(Å)	Ca R-factor (%)	Ti-O (Å)	Ti R-factor (%)	Fe-O (Å)	Fe R-factor (%)
Allende	2.780 (7)	11.6	2.008 (3)	5.8	2.021 (2)	4.9
Dar al Gani 456	2.665 (9)	1.9	1.903 (1)	2	2.016 (1)	0.67
L5 chondrite	2.639 (11)	6.7	1.906 (1)	3.8	2.086 (1)	9.4
Millbillillie	2.609 (4)	0.6	1.921 (4)	2.5	2.057 (1)	0.53

Table2. Chemical composition of bulk meteorites and tektite (by EPMA). Chemical composition of Dar al Gani 456 (L6 chondrite) is not published. As a reference, we used the chemical composition of other L6 chondrite.

Sample		SiO ₂ (wt%)	CaO (wt%)	TiO ₂ (wt%)	Al ₂ O ₃ (wt%)	FeO (wt%)	Reference
Allende		34.2	2.71	0.16	3.18	22.5	[1]
Dar al Gani 456	Feldspar	64.8	2.35	-	20.5	0.60	[11]
	Hollandite	63.8	2.92	-	20.7	1.01	
L5 chondrite	Oligoclase	63.4	2.41	-	22.4	-	[8]
	Chrysolite	36.0	-	-	-	24.6	
Millbillillie	Pyroxene	49.1-50.2	0.72-2.18	0.18-0.45	0.18-0.33	34.4-35.1	[14]
	Plagioclase	45.0-48.5	14.5-19.1	0.02-0.58	32.8-36.1	0.09-1.76	

Odessa	-	-	-	-	60.6-62.4	[3]
Australite	71.4-72.2	3.27-3.42	0.62-0.86	12.75-13.27	4.73-5.04	Measured
Impactite	65.3-68.3	0.01-0.20	19.1-20.5	0.01-0.02	0.06-0.84	[4]
Obsidian	68.16-69.1	2.36-3.32	14.94-15.32	0.7-0.81	2.64-3.23	Measured

4. Acknowledgment

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References

- [1] Elliott C J 1987 *Smithsonian Contributions of the Earth Science* **27** 49
- [2] El Goresy A and Fechtig H 1967 *Astrophys.* **11** 391
- [3] El Goresy 1967 *Geochemica et Cosmochimica Acta* **31** 1667
- [4] French B M, Koeberl C, Gilmour I, Shirey B, Dons J A and Naterstad J, 1997 *Geochimica et Cosmochimica Acta* **61** 873
- [5] Genge M J and Grady M M 1999 *Meteoritics and Planetary Science* **34** 341
- [6] Neuville D R, Cormier L, Flank A, Briois V and Missiot D 2004 *Chemical Geology* **213** 153
- [7] Mysen B and Neuville D 1995 *Geochimica et Cosmochimica Acta* **59** 325
- [8] Paris E, Romano C and Wu Z 1995 *Physica B* **208** 351
- [9] Seixas T M, Almeida B, Mendes M H, Salgueiro da Silva M A, Santos J F, Almeida F, Diogo Z, Lopes A B and Vieira JM 2013 *Materials Science Forum* **730-732** 170
- [10] Stebbins J F and McMillan P 1989 *American Mineralogist* **74** 965
- [11] Tobase T, Wang L, Yoshiasa A, Okube M, Nakatani T, Hayasaka Y and Isobe H 2013 *J. Phy. Conference Series* **430** 012070
- [12] Tomioka N, Mori H and Fujino K 2000 *Geophysical Research Letters* **27** 3997
- [13] Wang L, Yoshiasa A, Okube M and Takeda T 2011 *J. Synchrotron Radiation* **18** 855
- [14] Wang L, Yoshiasa A, Hiratoko T, Hu Y, Arima H and Sugiyama K 2013 *J. Mineralogical and Petrological Sciences* **108** 288
- [15] Yamaguchi A, Takeda H, Bogard D D and Garrison D 1994 *Meteoritics and Planetary Science* **29** 237
- [16] Yarger J L, Diefenbacher J, Smith K H, Wolf G H, Poe B and McMillan P F 1995 *Science* **270** 1964
- [17] Maeda H 1987 *Journal of Physical Society of Japan* **56** 2777