^{57}FE Mössbauer spectroscopy studies of Tektites from Khon Kaen, Ne Thailand

B. F. O. Costa · G. Klingelhöfer · E. I. Alves

Abstract Room temperature ^{57}Fe Mössbauer effect spectroscopy has been used to investigate the local Fe environment in a set of indochinite tektites from Thailand. A MIMOS II spectrometer in backscattering geometry has been used in the study, so that no sample preparation at all was required. The spectra have been analysed in terms of discrete spectral components using Voigt functions. The results are similar to those obtained with analysis done with quadrupole splitting distributions. In all cases the Mössbauer spectra show a broadened asymmetric quadrupole split doublet. The Fe^{2+} sites have been distinguished in Fe with octahedral and tetrahedral coordination. The Fe^{3+}/Fe^{2+} and Fe^{2+} tetrahedral/octahedral ratios have been determined from the relative areas of the various spectral components. Their values have been discussed in the light of actual literature.

Keywords Tektites · Natural glasses · Iron oxidation states

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1 Introduction

Tektites are glass beads, usually black or very dark, rarely more than a few cm in length, showing peculiar aerodynamic shapes and small pits which give hints to their formation. These glasses were for some time believed to may have originated from high-velocity volcanic material emitted from the Moon, escaping its gravitational field, and eventually landed on Earth [1]. Nowadays there is consensus that they are natural glasses originated from fused material spilled during a meteorite impact [2] a hypothesis which had already been defended by Faul [3], without the proper attention. Tektites found on land fall into three general morphological categories; splash-form tektites, aerodynamically shaped tektites and Muong Nong type tektites. The Muong Nong-type tektites differ from other forms by having irregular shapes and a layered structure. This has led to speculation that the Muong Nong-type tektites have been formed under somewhat different conditions than other tektites and likely formed closer to the center of the impact site [4, 5]

Tektites are found dispersed in well defined strewn fields: moldavites in Europe, around Moldavia, Czech Republic (the only ones that are light-green and translucent); bediasites and georgiaites in North America (Texas and Georgia, respectively); ivorites in Ivory Coast; tibetanites, chinites, indochinites, rizalites (from the Philippines), and australites, in the largest strewn field, which ranges from Tibet to the Antarctic Ocean [1].

High temperature processes in silicate glasses are followed by redox reactions involving variable-valence elements, iron in first. Study of valent and structural state of iron atoms can lead to a better understanding of the glasses formation process. Mössbauer spectroscopy is one of the most powerful methods for determination of the iron atoms valence and coordination [6, 7].

One particular feature commonly observed in tektites is an anomalously low Fe^{3+}/Fe^{2+} ratio [8] and this suggests that they were solidified in a low oxygen environment. Some evidence suggests that Muong Nong-type tektites may have a higher Fe^{3+}/Fe^{2+} ratio than splash form tektites and that this may be consistent with their general morphology and solidification from the melt at a lower temperature [9].

For the present work we have used Mössbauer spectroscopy to study Fe-site properties in a number of sub-spherical samples of indochinites, with diameters between 1.5 and 2.0 cm, collected near Khon Kaen, NE Thailand.

Early in the investigations of tektites, chemical analysis has been mainly used for determination of oxidation state of iron. The results of that kind of analysis became controversial and unreliable [10]. Some different chemical and instrumental methods have been used to prove usability of chemical analysis. Fudali et al. [11] used four wet chemical techniques (two standard volumetric methods, an experimental volumetric method for direct determination of Fe^{3+} and a colorimetric method) and two instrumental techniques (Mössbauer spectroscopy and electron spin resonance). They found that the Fe^{3+}/Fe^{2+} ratios are 0.02–0.12 and are in agreement with what they believe to be the best previously published analysis for tektites (review in [12]).

Another reason for inaccurate measurements of the iron oxidation state is the sample preparation. Usually the samples are cut and grinded in acetone or alcohol to prevent the contact with atmosphere. In our study we used the unique MIMOS II instrument operating in backscattering geometry to collect Mössbauer spectra, with no need of sample preparation.

In general, the results of Mössbauer effect spectroscopy for the analysis of Fe-oxidation state ratios in tektites depend critically on the method of spectral analysis. In recent years, more sophisticated and accurate methods of spectral analysis based on distributed hyperfine parameters, have been used by Dunlap and co-workers [13, 14] and Rossano et al. [15]. Those analyses gives consistently low values of the Fe^{3+}/Fe^{2+} ratio while an analysis using discrete spectral components, can yield anomalous results. In the present work we used discrete spectral components using Voigt functions for the analysis of the tektites spectra and the results were compared with the ones obtained by more sophisticated methods and found to be consistent with them.

2 Experimental procedure

The Khon Kaen indochinites, whose results are present in this study, have been all collected in the same location and are all identical. They were labeled accordingly to the recollection and storing, and we have kept their identification numbers in this paper. The samples were studied as a whole, without being cut, as Mössbauer spectra were recorded for all the samples at room temperature with a MIMOS II spectrometer [16] detecting 14.4 keV radiation in backscattering mode, and a $^{57}Co(Rh)$ source with an activity of about 30 mCi. No sample preparation was done to carry out the measurements. This is a big advantage relatively to the transmission geometry method, found in literature. In this later case, the sample needs to be cut and crushed into powder, with possible changes in oxidation ratios. The fitting procedure of the spectra was carried out using a set of Voigt lines and parameters determined by least squares method. For comparison, we have also used the NORMOS program as a fitting method of distribution of quadrupole splitting with a linear correlation between quadrupole splitting and isomer shift. The isomer shifts are given relative to α-Fe at RT.

3 Results and discussion

Room temperature ^{57}Fe Mössbauer spectra of the tektites are illustrated in Fig. 1, and their Mössbauer parameters are displayed in Table 1. In Fig. 1, it can be observed that for all the spectra there is a small misfit in the total fitted spectra for the more positive spectral component. This is possibly a result of constraints placed on the fitting parameters because of using Voigt functions.

^{57}Fe Mössbauer spectra of non-magnetic glasses have a characteristic form of asymmetrical, broad doublets. Broadening effects are important in glass spectra with line-widths as large as 0.6 mm/s against 0.3 mm/s in crystals.

All the spectra show the common feature having a strong quadrupole doublet with IS around 1 mm/s and QS around 1.9 mm/s, which are typical parameters for Fe^{2+} in octahedral coordination in tektites. The doublet corresponding to Fe^{2+} in tetrahedral coordination is not always seen in spectra of tektites. However some authors have seen it already, eg [14, 15, 17]. This same structure has been seen in the Mössbauer spectra of glassy andesite [18] and glassy basalt [19]. The values

Fig. 1 Room temperature
^{57}Fe Mössbauer backscattering
spectra of the tektites studied.
The fitresults to the spectra
are also shown (color on-line).
The codes shown on the left
side of each spectrum
are the names given
to the studied samples
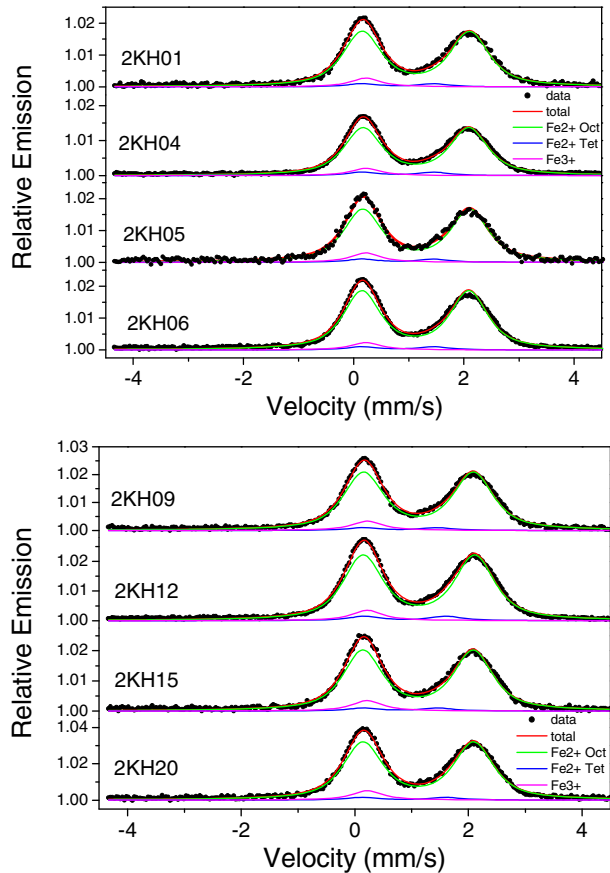
obtained by us (IS around 0.9 mm/s and QS around 1.3 mm/s) are higher than the ones obtained by Rossano and Dunlap for different tektites (IS around 0.6 mm/s and QS around 1 mm/s). Our values approach the ones obtained in other natural and synthetic glasses in which QS usually ranges between 1.4 and 1.8 mm/s [20]. The parameters obtained for the Fe^{3+} site, IS from 0.13 to 0.18 mm/s and QS of 0.02 mm/s, are in good agreement with the values referred in literature for tektites.

The site occupancy ratios agree in general with the ones obtained by Dunlap and Rossano.

The Fe^{2+}(tet)/Fe^{2+}(oct) ratio agree with the ratio for Rizalite tektites [13], Thailandites and Tibetanites [14]. The values obtained for Fe^{3+}/Fe^{2+} ratio are low and agree in general with the values obtained for tektites, in particular they are similar to the values obtained for Moldavite [13].

In the case of our tektites study, the oxygen partial pressure is presumably the most important factor in determining the Fe^{3+}/Fe^{2+} ratio, although chemical composition, maximum temperature and heating/cooling histories cannot be ruled out as possible contributing factors [13]. The larger Fe^{3+}/Fe^{2+} ratio obtained by us, relatively to the studies of Rossano and Dunlap for other tektites rather than the

Table 1 Hyperfine parameters for Fe^{2+} and Fe^{3+} sites and ratios of site occupancies in the tektites studied

	IS(mm/s)	QS(mm/s)	WID(mm/s)	%	$Fe^{2+}_{tetr}/$ Fe^{2+}_{oct}	$Fe^{3+}/$ Fe^{2+}
2KH01					0.049	0.070
Fe2+ Oct	1.14(1)	1.96(1)	0.65(1)	89.10		
Fe2+ Tetr	0.89(1)	1.30(1)	0.65(1)	4.36		
Fe3+	0.16(1)	0.02(1)	0.65(1)	6.54		
2KH04					0.063	0.066
Fe2+ Oct	1.14(1)	1.94(1)	0.65(1)	88.21		
Fe2+ Tetr	0.91(1)	1.30(1)	0.65(1)	5.57		
Fe3+	0.18(1)	0.02(1)	0.65(1)	6.22		
2KH05					0.051	0.072
Fe2+ Oct	1.16(1)	1.98(1)	0.65(1)	88.79		
Fe2+ Tetr	0.87(1)	1.30(1)	0.65(1)	4.49		
Fe3+	0.17(1)	0.02(1)	0.65(1)	6.72		
2KH06					0.048	0.073
Fe2+ Oct	1.13(1)	1.96(1)	0.65(1)	88.94		
Fe2+ Tetr	0.91(1)	1.30(1)	0.65(1)	4.29		
Fe3+	0.13(1)	0.02(1)	0.65(1)	6.77		
2KH09					0.041	0.074
Fe2+ Oct	1.14(1)	1.95(1)	0.65(1)	89.49		
Fe2+ Tetr	0.91(1)	1.30(1)	0.65(1)	3.63		
Fe3+	0.18(1)	0.02(1)	0.65(1)	6.88		
2KH12					0.058	0.066
Fe2+ Oct	1.14(1)	1.98(1)	0.65(1)	88.74		
Fe2+ Tetr	0.89(1)	1.44(1)	0.65(1)	5.11		
Fe3+	0.17(1)	0.02(1)	0.65(1)	6.15		
2KH15					0.043	0.077
Fe2+ Oct	1.13(1)	1.96(1)	0.65(1)	89.05		
Fe2+ Tetr	0.91(1)	1.30(1)	0.65(1)	3.80		
Fe3+	0.16(1)	0.02(1)	0.65(1)	7.15		
2KH20					0.040	0.071
Fe2+ Oct	1.14(1)	1.96(1)	0.65(1)	89.78		
Fe2+ Tetr	0.89(1)	1.48(1)	0.65(1)	3.60		
Fe3+	0.16(1)	0.02(1)	0.65(1)	6.62		

IS given relative to α-Fe at RT

ones mentioned above that give values closed to ours, suggests a greater oxygen partial pressure during formation of our tektites that also cause the Fe^{2+} to favor Fe^{2+} octahedral sites.

For comparison with the results obtained with the fitting carried out using Voigt functions, we fitted the spectra also using a distribution of QS with a linear correlation between QS and IS. The results obtained in this way, with our program, were not very satisfying. Although the parameters obtained for the main component of the spectra (the Fe^{2+} octahedral site) were in good agreement with the ones presented in Table 1, the Fe^{2+} tetrahedral component was not observed, and erroneous values of <QS> were obtained for the Fe^{3+} coordination site (values between 0.01 and 0.08 mm/s). The percentage obtained for this later site was found to be between 4 and 6 % of the total spectrum.

4 Conclusions

1. Our method of fitting tektites data with spectral components using Voigt functions, gives similar results as many other sophisticated methods used in recent years.
2. A distinction between tetrahedral and octahedral components of the Fe^{2+} sites is observed and this is consistent with other analysis using distribution parameters and analysis of spectra of glasses synthesized from silicate rocks with compositions that are similar to tektites.

References

1. O'Keefe, J.A.: Tektites and their origin. NASA Goddard Space Flight Center (1975)
2. Koeberl, C.: Geol. Soc. Amer. Spec. Pap. **239**, 133–151 (1994)
3. Faul, H.: Science **152**, 1341–1345 (1966)
4. McCall, G.J.M.: Tektites in the Geological Record: Showers of Glass from the Sky. The Geological Society, London (2001)
5. Koebert, C.: Geochim. Cosmochim. Acta. **56**, 1033 (1992)
6. Thorpe, A.N., Senftle, F.E., May, L., Barkatt, A., Adel-Hadadi, M.A., Marbury, G.S., Izett, G.A., Maurrasse, F.R.: J. Geophys. Res. **99**, 10881–10885 (1994)
7. Orkasson, N., Helgasson, O., Sigurdsson, H.: Geol. Soc. Amer. Spec. Pap. **307**, 445–452 (1996)
8. Chao, E.C.T.: The petrographic and chemical characteristics of tektites. In: O'Keefe, J.A. (ed.) Tektites, pp. 51. University of Chicago, Chicago, IL (1963)
9. Son, T.H., Koeberl, C.: Met. Planet. Sci. **46**(6), 805–815 (2005)
10. Volovetsky, M.V., Rusakov, V.S., Chistyakova, N.I., Lukanin, O.A.: Hypfine Interact. **186**, 965–970 (2008)
11. Fudali, R.F., Dyar, M.D., Griscom, D.L., Schreiber, H.D.: Geochim. Cosmochim. Acta **51**, 2749–2756 (1987)
12. Lukanin, O.A., Kadik, A.A.: Geochem. Int. **45**, 857–881 (2007)
13. Dunlap, R.A., Eelman, D.A., MacKay, G.R.: J. Non-Crystal. Solids **223**, 141–146 (1998)
14. Dunlap, R.A., Sibley, A.D.E.: J. Non-Crystal. Solids **337**, 36–41 (2004)
15. Rossano, S., Balan, E., Morin, G., Bauer, J.-P., Calas, G., Brouder, C.: Phys. Chem. Miner. **26**, 530–538 (1999)
16. Klingelhöfer, G., et al.: J. Geophys. Res. **108**, 8067 (2003)
17. Dunlap, R.A.: Hyperfine Interact. **110**, 217–225 (1997)
18. Dyar, M.D., Naney M.T., Swanson, S.E.: Am. Mineral **72**, 792 (1987)
19. Helgason, O., Steinthorsson, S., Morup, S.: Hyperfine Interact. **45**, 287 (1989)
20. Dickson, B.L., Smith, G.: Can. Miner. **14**, 206–215 (1976)