The chemical and mineral composition of volcanic ash in the Upper Carboniferous deposits of the Usolka section (South Ural, Russia)

R Kh Sungatullin1, G M Sungatullina1, F F Sadriev1, R N Aysina1

1Institute of Geology and Petroleum Technologies, Kazan Federal University, Kazan, Russia
E-mail: Rafael.Sungatullin@kpfu.ru

Abstract. Volcanic ash from the Usolka section, which is proposed as an international standard for global correlation of the lower boundaries of the Kasimovian and Gzhelian Stages, is considered. The content of rock-forming components in ashes is given. It is shown that the ashes of the Gzhelian Stage differ from older deposits in higher contents of Al, Ca, Mn and lower contents of Si, Ti, Fe. An increase in the content of some microcomponents (Cu, Cr, Ba, S) to the lower boundary of the Kasimovian Stage was noted. For the first time, information has been obtained on the mineral composition of ashes, which allows them to be used for correlation.

1. Introduction

The Usolka section is located on the right bank of the Yuryzan Usolka River in the Republic of Bashkortostan in the Southern Urals (Fig. 1). The coordinates of the section: 53 ° 55´28´´N, 56 ° 31´47´´E. This section has been proposed as a candidate of the Global Boundary Section Stratotype and Point (GSSP) for the base of the Gzhelian Stage in the International Stratigraphic Chart. The Usolka section was demonstrated as a potential GSSP at the summer of 2015 to participants in the field excursion of the XVIII International Congress on the Carboniferous and Permian [5]. The section is represented by terrigenous-carbonate rocks of Carboniferous (Moscovian, Kasimovian, Gzhelian Stages) and Permian (Asselian, Sakmarian Stages) with intercalations of volcanic ash. This allowed to obtain here detailed dates on the absolute age of zircons from ash horizons by the mass spectrometric method with thermal ionization and isotopic dilution — ID-TIMS [4]. Today, these data are used in the International Chronostratigraphic Scale [3], because they provide high resolution (~ 0.1 Ma) for the Carboniferous and Permian interval as an important complement to the global biostratigraphic correlation. Detailed biostratigraphic characteristics of the Usolka section are given in [1, 2, 7-9].

This research is devoted to the analysis of the chemical, mineral, and particle size composition of the ash horizons of the Usolka section. Volcanic ashes are found in the form of interlayers of small thickness - from 1-2 to 8 cm, they have yellowish to dark brown shades that contrastly distinguish...
them against the background of gray and light gray host rocks (Fig. 1). The interlayers of the volcanic ashes are composed of finely dispersed clay particles, sometimes cemented by iron hydroxides (Fig. 1, below). We selected 17 samples from the ash horizons of Carboniferous deposits (Fig. 2): the Upper Moscovian, Kasimovian and Lower Gzhelian Stages. The absolute age of this interval is \( \approx 302-307.5 \) million years for U-Pb dating of zircons in the Usolka section [3, 4].

Figure 1. Usolka section.
   a - Kasimovian deposits (photo of S.S. Sukhov);
   b - c - thin sections from ash horizons: b - Kasimovian Stage (U-6); c - Gzhelian Stage (U-15)
3. Methodology

To determine the chemical composition of the samples, X-ray spectral fluorescence analysis was performed using a S8 Tiger wave dispersive X-ray fluorescence spectrometer (Bruker, Germany). To establish the mineral composition of ash horizons, an analysis was performed using a Bruker D2 Phaser X-ray diffractometer (Germany) with a copper and cobalt anode. Granulometric analysis of samples was performed. All analyzes were performed in the laboratories of KFU, analysts G. M. Eskina, B. I. Gareev, G. A. Batalin. Processing the results of chemical analyzes in the work was carried out by methods of mathematical statistics using the software packages STATISTICA and Excel.

3. Results and Discussions

According to the results of X-ray phase analysis, kaolinite, montmorillonite, and quartz are present in all ash samples (fig. 3). Often calcite, muscovite (absent in sample U-3) and albite (absent in sample U-10) are common. Clinohornblende and microcline are found in three samples (U-1, U-3, U-10). In 2 samples, dolomite (U-1 and U-13) and hornblende (U-10 and U-16) were found. Based on the results obtained, we can conclude that in the upper part of the Moscovian and Kasimovian Stages there is a wider range of minerals, which can be used as a mineralogical correlation criterion.

Analysis of the particle size distribution showed that in the ashes dominated (about 70%) particles of the silt fraction (0.1-0.01 mm). The clay fraction (<0.01 mm) is 20-30%, while the sand fraction (> 0.1 mm) accounts for 10-15%.
Figure 3. The mineral composition of ash horizons.

| Sample number (Stage) | Quartz | Calcite | Kaolinite | Muscovite | Albite | Dolomite | Montmorillonite | Kliinochlor | Microline | Hornblende |
|-----------------------|--------|---------|-----------|-----------|--------|-----------|----------------|-------------|------------|------------|
| U-16 (Gzhelian)       |        |         |           |           |        |           |                 |             |            |            |
| U-13 (Kasimovian)     |        |         |           |           |        |           |                 |             |            |            |
| U-10 (Kasimovian)     |        |         |           |           |        |           |                 |             |            |            |
| U-3 (Kasimovian)      |        |         |           |           |        |           |                 |             |            |            |
| U-1 (Moscovian)       |        |         |           |           |        |           |                 |             |            |            |

Figure 4. Comparison of average component contents (wt.%) in ash horizons. 
TiO$_2$ content is increased 10 times, MnO - 100 times.
From the chemical analysis of the ash horizons (table), it can be concluded that the predominant components are (in decreasing order) silica, alumina and iron. Comparison of the average content of components in the ash horizons (fig. 4) showed that the ashes of the Gzhelian Stage ashes differ from Moscovian and Kasimovian deposits in higher contents of Al, Ca, Mn and lower contents of Si, Ti, Fe. This is probably due to the difference in the composition of the volcanic material that entered the marine basin at the end of the Carboniferous period. In the Moscovian and Kasimovian Age, the composition of volcanics was intermediate and mafic (see table), while in the Gzhelian Age the ultramafic composition of volcanics predominated, which is also indicated by the presence of hornblende (see fig. 3). A joint analysis of silica, alumina and calcium showed (fig. 5) that volcanic ash forms a separate field outside the general trend of flysch rock formations. An increase in the content of some microcomponents (Cu, Cr, Ba, S) at the base of the Kasimovian Stage (fig. 6) was also noted, which can be used as a geochemical criterion for correlation of sections.

**Figure 5.** The chemical composition of the ash horizons and flysch formation in the Upper Carboniferous interval of the Usolka section.
Table. Chemical composition of the Carboniferous rocks of Usolka section, weight %.

| Sample | SiO₂ | TiO₂ | Al₂O₃ | Fe₂O₃ | Cr₂O₃ | MnO | MgO | CaO | Na₂O | K₂O | P₂O₅ | SrO | BaO | SO₃ | NiO | CuO | ZnO | Ga₂O₃ | As₂O₃ | SeO₂ | Rb₂O | Nb₂O₃ | ZrO₂ | LOI |
|--------|------|------|-------|-------|-------|-----|-----|-----|-----|-----|------|-----|-----|-----|-----|-----|-----|------|------|------|------|------|------|-----|
| U-1    | 52.92| 0.68 | 14.85 | 6.45 | 0.04  | 0.01| 2.49| 2.02| 0.40| 3.72| 0.17 | 0.01| 0.04| 0.31| 0.03| 0.01| 0.02| 0.01 | 0.002 | 0.003 | 0.01 | 0.02 | 15.79 |
| U-2    | 48.9 | 0.39 | 15.94 | 6.17 | 0.04  | 0.01| 3.21| 4.07| 0.24| 2.74| 0.53 | 0.01| 0.05| 0.12| 0.04| 0.01| 0.04| 0.01 | 0.003 | 0.003 | 0.01 | 0.006 | 17.44 |
| U-3    | 47.3 | 0.31 | 17.35 | 5.89 | 0.015 | 0.01| 2.84| 0.92| 0.23| 3.00| 0.07| 0.005| 0.04| 0.03| 0.01| 0.02 | 0.002 | 0.003 | 0.004 | 0.01 | 0.01 | 21.89 |
| U-4    | 66.67| 0.19 | 9.05  | 3.98 | 0.01  | 0.01| 0.74| 0.58| 1.22| 0.79| 0.07| 0.01| 0.05| 0.1  | 0.02| 0.01| 0.01 | 0.002 | 0.002 | 0.009 | 0.01 | 0.01 | 16.48 |
| U-5    | 63.89| 0.16 | 10.85 | 3.02 | 0.01  | 0.01| 1.09| 0.57| 1.79| 1.20| 0.03| 0.01| 0.05| 0.1  | 0.01| 0.01| 0.01 | 0.001 | 0.001 | 0.10  | 0.01 | 17.24 |
| U-6    | 66.43| 0.35 | 10.53 | 3.29 | 0.01  | 0.01| 1.73| 0.67| 0.55| 1.81| 0.05| 0.01| 0.04| 0.01 | 0.01| 0.01| 0.01 | 0.001 | 0.001 | 0.01  | 0.01 | 14.44 |
| U-7    | 56.66| 0.45 | 14.61 | 5.15 | 0.03  | 0.01| 2.76| 1.16| 0.45| 2.69| 0.11| 0.01| 0.03| 0.08 | 0.03| 0.01| 0.04 | 0.003 | 0.003 | 0.006 | 0.02 | 15.68 |
| U-8    | 49.73| 0.34 | 16.4  | 4.94 | 0.02  | 0.01| 2.97| 2.47| 0.31| 2.42| 0.10| 0.01| 0.05| 0.07 | 0.02| 0.01| 0.03 | 0.002 | 0.002 | 0.004 | 0.01 | 0.01 | 20.06 |
| U-9    | 50.04| 0.37 | 19.92 | 5.48 | 0.01  | 0.01| 2.77| 2.07| 0.30| 2.68| 0.07| 0.01| 0.08| 0.05 | 0.03| 0.01| 0.02 | 0.002 | 0.003 | 0.01  | 0.01 | 16.02 |
| U-10   | 44.65| 0.26 | 19.51 | 6.40 | 0.01  | 0.02| 3.32| 4.07| 0.13| 2.46| 0.05| 0.01| 0.05| 0.05 | 0.04| 0.01| 0.02 | 0.002 | 0.002 | 0.02  | 0.01 | 18.91 |
| U-11   | 48.75| 0.4  | 18.24 | 5.55 | 0.01  | 0.01| 2.9 | 1.83| 0.29| 2.78| 0.08| 0.01| 0.11| 0.09 | 0.03| 0.01| 0.02 | 0.002 | 0.003 | 0.01  | 0.01 | 18.86 |
| U-12   | 48.8 | 0.48 | 19.95 | 7.82 | 0.03  | 0.01| 2.91| 1.41| 0.27| 3.11| 0.09| 0.004| 0.66 | 0.14| 0.05| 0.01| 0.04 | 0.002 | 0.004 | 0.01  | 0.02 | 14.83 |
| U-13   | 43.34| 0.66 | 12.36 | 5.78 | 0.11  | 0.02| 2.67| 5.93| 0.48| 3.25| 0.59| 0.01| 0.09| 0.83 | 0.04| 0.12| 0.001| 0.003 | 0.01  | 0.01 | 23.60 |
| U-14   | 40.15| 0.25 | 16.22 | 5.33 | 0.01  | 0.04| 2.97| 4.71| 0.12| 2.24| 0.05| 0.01| 0.2 | 0.08 | 0.05| 0.01| 0.04 | 0.002 | 0.01  | 0.01 | 27.48 |
| U-15   | 47.69| 0.36 | 18.83 | 6.05 | 0.01  | 0.03| 2.94| 1.74| 0.33| 2.75| 0.09| 0.01| 0.02| 0.06 | 0.04| 0.01| 0.03 | 0.001 | 0.004 | 0.01  | 0.01 | 18.99 |
| U-16   | 47.89| 0.43 | 20.00 | 8.44 | 0.02  | 0.01| 2.86| 1.76| 0.29| 2.8 | 0.10| 0.01| 0.02| 0.14 | 0.07| 0.01| 0.04 | 0.002 | 0.003 | 0.01  | 0.02 | 15.08 |
| U-17   | 58.15| 0.51 | 12.79 | 6.84 | 0.03  | 0.04| 2.08| 3.45| 0.72| 2.54| 1.60| 0.03| 0.14| 0.05 | 0.01| 0.09 | 0.001 | 0.004 | 0.004 | 0.01 | 0.01 | 10.83 |
Figure 6. Distribution of copper and barium in the ash horizons of the Usolka section.
Conclusions

1. The chemical and mineral composition of the ash horizons of the Upper Carboniferous deposits of the Usolka section has been studied for the first time.

2. It was established that in the ash horizons the silt fraction prevails, clay and a slightly sandy fraction are less developed.

3. The main minerals of ash include kaolinite, montmorillonite, quartz, which confirms their volcanic origin.

4. Chemically, ash horizons consist of siliceous, clayey and calcareous materials, which indicates their polygenic volcanic-sedimentary origin.

5. The studied horizons can be good lithological, mineralogical, and geochemical markers for correlation of sections of the Upper Carboniferous of the Urals.

Acknowledgements

The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University.

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