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TRANSFORMATION OF THE INITIAL ISOTOPIC COMPOSITION OF PRECIPITATION IN CAVES OF THE SOUTH-WESTERN CAUCASUS

ABSTRACT. The paper presents preliminary results and interpretation from an ongoing research project in the Novy Afon and Abrskil caves of Abkhazia. The research have demonstrated that $\delta^{18}O$ and δD analyses of drip and ground waters in two caves in the South-Western Caucasian region allows to better understand interaction between isotopic composition of precipitation, soil, and vadose zone. Drip and ground water samples from the caves were compared with the present-day Global (GMWL) and the Local Meteoric Water Lines (LMWL). They fall along the GMWL and LMWL and are tied by equation $\delta D = 5.74\delta^{18}O - 6.98$ ($r^2 = 0.94$). Drip water isotopic composition is similar to that from lakes and pools. The incline of $\delta^{18}O - \delta D$ line differs from GMWL and LMWL. It reflects a possible result from secondary condensation and evaporation and water-rock interaction, and depends on the climate aridity level.

KEY WORDS: Caucasus, cave, isotopes, paleoclimate, ground water.

INTRODUCTION

Understanding of recent climate change, its regional patterns, origin, and prediction is currently a major scientific challenge. Networks of climatic proxies with annual resolution, covering the areas of continental scale, can provide data for statistical analyses and numerical modeling of past climate change and thereby improve climate projections for the future. Calcareous speleothems provide continuous paleoclimate records for 10^3–10^5 years. The most extensively used speleothem paleoclimate proxies are carbon and oxygen isotopes. Significant progress in using the stable isotopic composition in speleothems has been made in the past few decades [e.g., Affolter et al., 2014; Boop et al., 2014; Fairchild et al., 2006; McDermott, 2004 and references cited therein]. Recently, Vasil'chuk and Vasil'chuk [2011] summarized previous studies on the stable water isotopic composition of cave ice and have shown that $\delta^{18}O$ and δD analyses of the cave ice reflect the input isotopic signal of the local rain water. Numerous studies have been focused on monitoring changes of precipitation water isotopic composition due to interactions in the soil and vadose zone and within the caves [Petrella, Celico, 2013; Bradley et al., 2010; Barnes, Allison, 1988]. Some results [e.g., Cuthbert et al., 2014: Luo et al., 2013] were calibrated by meteorological records.

Here, we report the results of measurements of the stable isotopic composition of drip water, cave pool water, and rain water samples from the Novy Afon and Abrskil caves in Abkhazia. We have extended the approach by adding the groundwater isotope component and comparing it with the Caucasus mountain glacier isotope composition in order to understand the processes controlling drip water and ground water isotopic composition at the studied sites.

SITE BACKGROUND

Data of environmental and climatic change in Abkhazia are presented in dendrochronological, paleolimnological, glaciological, and speleological archives as well as in historical record of climatic events in the past. High-resolution paleoclimatic reconstructions are lacking for this area, but a number of similar reconstructions developed for the cross-border region of Northern Caucasus [Solomina et al., 2012, 2014; Dolgova et al., 2013] may be applied for the Abkhazia area. Karst systems are abundant in the region due to specific geological and tectonic conditions. Cave calcites and stalagmites, in particular, may contain valuable paleoclimatological information. We have selected two caves for our reconnaissance study in Abkhazia.

The study areas are located in the central and eastern parts of Abkhazia (Fig. 1). The two studied caves are the Novy Afon and the Abrskil. The sampling sites are shown in Figure 1.

The entire study area is located in the south-western part of the Greater Caucasus Range

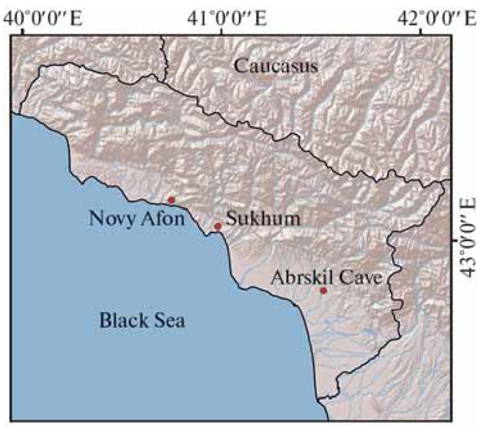

Fig. 1. Geographical location of sampling sites

(Fig. 1). The north-western and northern boundaries follow the Psou river-valley and the main ridge of the Greater Caucasus. Abkhazia has a joint border with Georgia on the east; it is bound by the Black Sea on the south and southwest. Its west-east and north-south extend is 170 km and 66 km, respectively, with the total area is 8665 км^2 [Ekba, Dbar, 2007]. The coastal range zone is situated between the marine plain and the belt of mid-mountain ranges located at the foothills and southern slopes of the Gagr, Bzyb, Abkhaz, and Kodor Ranges. Calcareous rocks and massive carbonates are widespread. This area is generally influenced by westerly circulation, however, the Greater Caucasian Range blocks penetration of cold air masses from the north. The mean annual air temperature at the Sukhum meteorological station (75 m a.s.l.) for the period 1904–2012 is 14.7 °C, while the mean winter (November–March) and summer (April–October) temperature is 7.0 °C and 22.7 °C, respectively. Mean annual precipitation for the same period is 1550 mm a^{-1} (870 mm a^{-1} in summer and 680 mm a^{-1} in winter).

KARST CAVES IN ABKHAZIA

More than 500 caves and carbonate caverns are located throughout Abkhazia [Tintilozov, 1976; Ekba, Dbar, 2007]. Abundant karst system and vauclusian springs are widespread near Mt. Iverskaya (344 m a.s.l.) and Mt. Novy Afon (500 m a.s.l.), and in the Psyrtsha river basin. The largest know Novy Afon (NA) cave and the underground Psyrtsha river represent the joint hydrogeological system. The cave is located in the interior of Mt. Iverskaya (344 m a.s.l.). The cave developed in the 300-meter depth Lower Cretaceous carbonates and was known from ancient times. It has been formed in the crest position of an anticlinal structure with permanent fold intensity and significant openness of fractures [Ekba, Dbar, 2007]. This cave system hosts abundant calcite dripstones many of which are currently actively forming. Considerable part of the NA cave has been recently adapted as a show cave for tourist activity. The cave entrance is situated at an elevation of 220 m. The total length of the cave passages is 3285 m, floor area is about 50 000 m^2, the height of the cave extension ranges between 15 and 67 m, the width varies from 20 to 70 m, and the total volume is $1.5 \cdot 10^6$ m^3 [Tintilozov, 1983].

Air exchange, defining the cave climatology, has been accelerated after the artificial tunnel and chamber construction. The approach of Ekba and Dbar (2007) provided for air ventilation in the NA cave that is influenced by air pressure at the surface of the karst massif. Air temperature measurements at the Novy Afon meteorological station show seasonal variations of average monthly temperature of 14–18 °C, while seasonal changes in the cave air temperature range between 0.2 and 1.2 °C for the 2004–2005 period. Temperature variability in the cave is within the range of 12.6–14.4 °C. Relative humidity in the cave was recorded over the 1970–1973 period; it varies from 98 to 100%, consistent with the cave ventilation and the outside air temperature.

The Abrskil cave is located in the eastern part of Abkhazia in the piedmont of the Panavsky Range (Fig. 1). The extension of explored part of the cave is 2700 m. The measured air temperature ranges from 12 to 14 °C.

SAMPLING SITES

Our monitoring research was undertaken at the Novy Afon and Abrskil caves in Abkhazia, South Western Caucasus (Fig. 1). Six samples were collected in the Novy Afon cave, including lake water, pool water, and drip water (Fig. 2). Also, drip water was collected in the Abrskil cave. Water isotopic composition of the Anakopia well water and rain water samples were analyzed for comparison with the cave water content.

The Anakopia well is located at the top of Mt. Iverskaya. The temple and the fort royal, awhile later, were built at the mount summit in the VI–VII centuries. They were mentioned in the medieval Georgian chronicle of the XI century where the battle with the Arabs in the 30s of the VIII century was reported. The temple was rebuilt several times; the last renovation was done by monks of the Novy Afon monastery in the beginning of the XX century when the ancient tanker well was cleared and reconstructed (http://afon-abkhazia.ru/). The well was cut in the rock and the pit of 1 m in diameter and 25 cm deep was found.

Rainfall water was sampled on September, 2014, in the on-shore area near Novy Afon at 5 m above sea level.

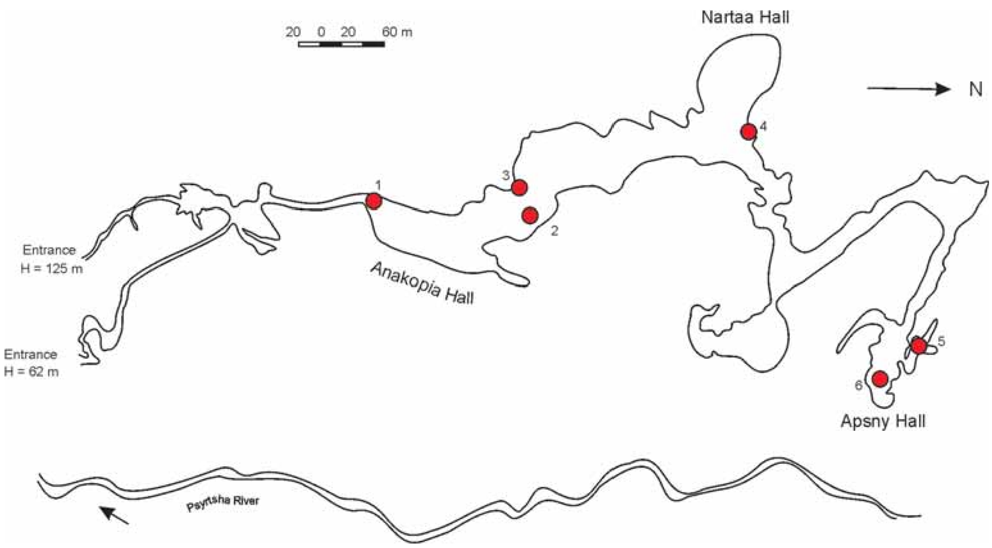

Fig. 2. Novy Afon Cave sampling locations (modified from: Tintilozov, 1983). Site numbers are given in Table 2.

METHODS

Drip and vadose waters as well as rainfall water were analyzed for the deuterium-hydrogen (D/H) and oxygen ($^{18}O/^{16}O$) isotope ratios using Picarro L1102-I instrument in the Climate and Environment Research Laboratory (CERL), Arctic and Antarctic Research Institute, St. Petersburg, Russia. To estimate precision of the measurements and to minimize memory effect associated with continuous measurements, the instrument was calibrated on a regular basis against isotopic standards V-SMOW, GISP, and SLAP provided by the International Atomic Energy Agency (IAEA). The estimated accuracy was ±0.05‰ for oxygen isotope ($\delta^{18}O$) and ±0.70‰ for deuterium (δD). The CERL laboratory working standard SPB was measured repeatedly following analysis of every 5 samples. The $\delta^{18}O$ and δD values were expressed in‰ units relative to the V-SMOW value.

RESULTS AND DISCUSSION

Isotopic composition of precipitation reflects the initial climatic signal. Evaporation of rainfall waters during infiltration into the upper vadose zone leads to their enrichment with heavy D and ^{18}O isotopes [Bar-Matthews et al., 1996; Ferronsky, 2015]. We are particularly interested in the mixture of isotopically modified rain waters and cave waters during stalagmite formation. The enrichment level of ground waters with heavy D and ^{18}O isotopes is the regional response and depends mainly on climate aridity. Independent study of isotopic composition of cave waters and precipitation is an essential component of cave speleothem research.

The use of oxygen ($\delta^{18}O$) and hydrogen (δD) isotopic composition allows obtaining additional information on transformation of precipitation. On the global scale, this is represented by the global meteoric water line (GMWL) relationship: $\delta D = 8\delta^{18}O + 10$ [Craig, 1961]. It may vary in local and regional conditions. As for ground waters, the incline of the curve at $\delta^{18}O$ – δD diagram describes the level of postdepositional transformation in precipitation.

Currently, there are very few $\delta^{18}O$ – δD records available for the Caucasus [Vasil'chuk et al., 2006; Kutuzov et al., 2014] and these data have been obtained in glacierized areas. We included $\delta^{18}O$ – δD precipitation records derived at the GNIP (Global Network of Isotopes in Precipitation, IAEA) stations in the Caucasus and Black Sea region as well as snow and ice isotopic composition records from the Elbrus and Kazbek volcanic massifs (Table 1) in our study.

Figure 3a shows that δD and $\delta^{18}O$ data from precipitation and glacier ice plot near or on the bottom right of the GMWL from the isotopic data in the lowland sites (Batumi,

Table 1. The GNIP station and the Northern Caucasus water isotopic sampling sites.
For each site, $\delta D = a\,\delta^{18}O + b$ relationship is shown.
The source for the GNIP sites: http://www.univie.ac.at/cartography/project/wiser/gui/gnip

GNIP code	Co-untry	Station name	Latitude	Longitude	Eleva-tion, m	Period of observa-tion	$\delta D = a\,\delta^{18}O + b$	R^2
3748400	Georgia	Batumi	41° 39′00″	41° 38′0″	6	1980–1990	y = 7,3519x + 9,1406	0,86
3752400	Georgia	Bakuriani	41° 42′36″	43° 30′36″	1665	2007–2009	y = 7,6565x + 11,311	0,98
3754900	Georgia	Tbilisi	41° 40′48″	44° 57′00″	490	1969–2009	y = 7,3339x + 6,0245	0,98
170260	Turkey	Sinop	42° 1′30″	35° 9′30″	32	1966–2009	y = 6,1343x – 1,2276	0,956
3473100	Russia	Rostov-na-Donu	47° 15′00″	39° 49′12″	77	1970–1990	y = 7,3843x + 3,0123	0,90
	Russia	Elbrus	43° 20′53.9″	42° 25′36.0″	5115	2012–2013	y = 7,8966x + 17,475	0,99
	Russia	Kazbek	42° 42,190′	44° 29,917′	4700	2013–2014	y = 8,0843x + 18,417	0,99

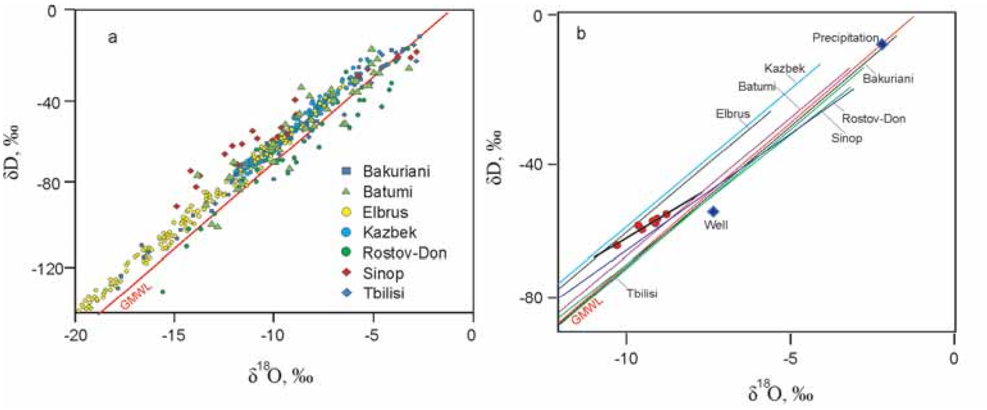

Fig. 3. (a) δD vs. δ18O for monthly precipitation at the GNIP stations and isotopic composition of the ice cores from the Caucasian glaciers. Global Meteoric Water Line (GMWL) (red line) is shown. (b) Trend lines of the data presented in (a): GMWL (red line) and δD vs. δ18O regressions for each site, drip water and ground water samples from the Novy Afon and Abrskil Caves (red circles) and δD vs. δ18O regression (black line), rainfall on September 9, 2014 and Anakopia Well samples (blue diamonds). Regression equations and correlation coefficients are presented in Table 1

Rostov-na-Donu), but near or on the top left in the mountain regions. McGarry et al. (2004) arrived at a similar result in the Eastern Mediterranean where the local meteoric water lines (LMWL) are ranged depending on air temperature and relative humidity. The δD and δ^{18}O record of rain precipitation collected on 9 September 2014 at sea level near the Novy Afon plots on the GMWL (blue diamond on Fig. 3b). The figure shows that isotopic composition of precipitation agrees completely with the regional pattern.

The δ^{18}O and δD values in all ground waters including drip water, cave lakes, and small pools vary within a rather small range from –10.23‰ to –8.88‰ and from –66.23‰ to –58.07‰, respectively (Table 2). Figure 3b demonstrates that the ground water samples fall along the GMWL and LMWLs with equation $\delta D = 5.74\ \delta^{18}O - 6.98$

Table 2. Water isotopic composition

Sample number	Location	δ^{18}O,‰	δD,‰
1	N. Afon, Anakopia Hall, lake water	–9,64	–61,12
2	N. Afon, Anakopia Hall, pool water	–9,18	–60,38
3	N. Afon, Anakopia Hall, drip water	–8,88	–58,07
4	N. Afon, Nartaa Hall, lake water	–10,23	–66,23
5	N. Afon, Apsny Hall, drip water	–9,24	–59,75
6	N. Afon, Apsny Hall, pool water	–9,11	–59,33
7	Abrskil, drip water	–9,54	–61,93
8	Rainfall (09/09/14)	–2,24	–7,35
9	Anakopia Well	–8,27	–52,57

(r^2 = 0.94). Drip water isotopic composition is similar to that from lakes and pools. The incline of $\delta^{18}O - \delta D$ line differs from GMWL and LMWL. It reflects a possible result from secondary condensation and evaporation and water-rock interaction, and depends on climate aridity level. The value of the coefficient **a** in $\delta^{18}O - \delta D$ relationship is 2.9 ± 0.2 for extra arid conditions of Northern Africa [Gonfiantini et al., 1974]. It ranges from 4 to 6 for the cave waters in South East China and Western Australia [Couthbert et al., 2014; Luo et al., 2013]. However, McGarry et al. (2004) observed $\delta^{18}O - \delta D$ relationship in the Soreq cave, Israel, which is close to the Mediterranean Meteoric Water Line with a similar **a** coefficient.

This result shows the extent of atmospheric precipitation transformation under infiltration through the vadose zone in the south-west Caucasus. It is necessary to explore the reliability of this relationship in the annual and interannual cycle.

The δD and $\delta^{18}O$ composition of water in the Anakopia well at the top of Mt. Iverskaya shows (Fig. 3b, blue diamond) the discrepancy with the regional precipitation isotopic content. The water level in the well is permanent over the whole year; however, the drainage area is not sufficient for maintenance of the stable level because of rain water input. Isotopically, it is consistent with ground waters from the Novy Afon and Abrskil caves (see Table 2). This shows that cave and fault-line waters are considerably concerned with the Anakopia well water.

CONCLUSIONS AND FUTURE WORK

The speleothem water isotopic composition, originally sourced from precipitation, may change due to evaporation in the soil and vadose zone and in the caves. Transformation of the initial isotopic composition depends on climate aridity. At our monitoring sites, drip and ground waters were heavier than precipitation near the cave area and the weighted mean regional precipitation. Our first approach provides the basis for exploring the relationship between the speleothem water isotopic composition and the corresponding precipitation waters. However, many problems of the speleothem application as paleoclimate indicators have not been taken into account in our research. The oxygen isotopic composition in different drip waters within the same cave can be effected by hydrological processes and can differ from site to site. High temporal resolution drip rate monitoring has to be combined with monthly isotope drip water and rainfall sampling at the Novy Afon cave. It is necessary to explore monthly isotopic composition in precipitation and establish the relationship with air temperature. This would provide for interpretation of speleothem water isotopic records in terms of temperature changes at the surface.

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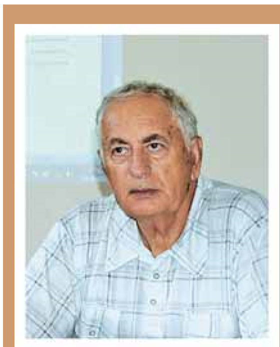

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