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Rainfall and hydrological controls on speleothem geochemistry during climatic events (droughts and typhoons): An example from Seopdong Cave, Republic of Korea

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ABSTRACT

A five year-old, 20 cm-long soda straw (SD-1) was analyzed geochemically to delineate the relationship between the geochemical record and climatic behavior. The growing tip of the soda straw was marked on July 18, 1999, and the sample was collected on July 16, 2004, thus the growth period of this speleothem is well constrained. During the five years the soda straw grew about 20 cm, a mean growth rate of about 4 cm/year. Fast growth rate of this speleothem enabled not only to understand seasonal variations of geochemical data but also to compare these data directly with outside climatic variations near the cave. $^{210}Pb_{ex}$ (excess or unsupported ^{210}Pb) results suggest that the overall pattern of $^{210}Pb_{ex}$ changes as well as the frequency and relative intensity of their peaks show a strikingly similar pattern to that of the amounts of precipitation in the study area. This suggests that $^{210}Pb_{ex}$ was transported into the cave with infiltrating rainwater mostly during rainy summers because $^{210}Pb_{ex}$ is a particle-reactive element. Controlling detailed growth rates by the $^{210}Pb_{ex}$ fluctuations, it can be noticed that $\delta^{18}O$ compositions vary very little in spite of significant droughts and typhoon events, whereas $\delta^{13}C$ values clearly display impacts of a severe drought from 2000 to 2001. The Sr/Ca, Ba/Ca, U/Ca and Mn/Ca ratios coincide with the $\delta^{13}C$ trends and show anomalies during the drought period. These coeval trends strongly indicate that hydraulic factors in vadose zone that were directly controlled by the amount of rainfall, influenced on the geochemical imprints of the SD-1. This study illustrates the behavior of an atmospheric radionuclide ($^{210}Pb_{ex}$), the O and C stable isotopes and trace elements in calcite speleothems and, furthermore, implies that they can be used to detect short-term climatic behavior, including climatic extreme events, as well as the long-term climatic fluctuations in the past.

1. Introduction

Recent investigations by carefully designed monitoring of waters in limestone caves and with artificially precipitated speleothems have contributed significantly to speleothem paleoclimatic research (e.g. Huang and Fairchild, 2001; Spötl et al., 2005; Baldini et al., 2006; Mickler et al., 2006). However, it is still necessary to trace the signals of serious climatic events with socioeconomic impacts from the speleothems with well constrained ages to use speleothems as significant paleoclimatic proxies for better paleoclimatic interpretations. Therefore, the geochemical data obtained in modern speleothems should be compared to available meteorological and historical data to further study the links with climate and to establish a reliable scientific base (e.g., Treble et al., 2003; Verheyden, 2004; Desmarchelier et al., 2006; Fairchild et al., 2006).

In this respect, several studies have shown that trace element contents (especially Sr, Ba, Mg, and U) in speleothems that grew past a few decades show distinctive seasonal variations (e.g. Treble et al., 2003; Kuczumow et al., 2005; Desmarchelier et al., 2006). However, several unsolved issues are still remained. For instance, although oxygen isotope compositions of incoming cave water do not vary much seasonally due to mixing of rainwater with groundwater in epikarst (Ford and Williams, 2007), recent oxygen isotope values of speleothems confirmed typhoon records for short intervals (Frappier et al., 2007). Thus, it is necessary to collect various data from many areas and to understand hydraulic and geochemical processes in epikarst regions to solve this discrepancy. It is also necessary to understand how carbon isotopes, trace elements, soil-derived organic matter, volcanic ash and atmospheric radionuclide may reflect recent climatic events and what kind of climatic factors are responsible to control these geochemical proxies.

Speleothems such as stalagmites, flowstones and stalactites have been used for paleoclimatic research until recently. However, because other common speleothems in limestone caves such as soda straws,

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draperies, cave corals contain laminated texture with growth, they may retain textural and/or geochemical proxies that can be quite sensitive to climatic fluctuations outside. Especially, soda straws were used quite efficiently for paleoclimatic research and cave monitoring due to their distinctive growth laminae, continuous growth and relatively faster growth rate (Desmarchelier et al., 2006).

Here we report results for one soda straw that grew over a five years period during which local meteorological instrumental records were recorded and climatic extreme events occurred. It is the objective of this study to show the behavior of geochemical proxies interpreted at seasonal resolution from the soda straw. This result can provide invaluable information on the application of paleoclimatic investigation using speleothems for longer as well as shorter periods of geological time.

2. The cave setting and speleothem sample

Seopdong Cave is located in the central part of the Korean peninsula (Fig. 1). The cave was discovered during past mining operations, and is a typical limestone cave about 700 m long (Fig. 2). It is formed in the Ordovician Jeongseon Formation (Joseon Supergroup) that is mostly composed of limestone with thin beds of dolomite (Cheong et al., 1979). Korean peninsula is located in temperate climate region and is influenced by East Asian Monsoon climate showing hot/humid summers and cold/dry winters (Fig. 3). Most of annual precipitation (50 to 60%) is concentrated between June and September, and the peninsula is directly or indirectly affected by tropical typhoons at least two to three times every year (Korea Meteorological Administration, http://www.kma.go.kr). Averaged annual temperature in central Korea (from Wonju Meteorological Station which is about 42 km away from Seopdong Cave) based on the instrumental records from 1971 to 2000 is 10.8 °C and the total amount of annual precipitation is 1290.9 mm.

SD-1 is a soda straw that grew about 204 m from the cave entrance and about 60 m beneath the overlying surface (Figs. 2 and 3). Soda straw is one of common speleothems formed by dripping water in many limestone caves. The inside is usually an empty tube, although they may become partially filled with calcite crystals. The water for the growth is supplied through the central canal and soda straws always hold a water drop on the tip. Carbon dioxide degasses continuously from the water drop and calcite is precipitating at its tip (Hill and Forti, 1997). The tip of growing soda straw studied was carefully marked in red with a red marker pen on July 18, 1999 and the sample was collected on July 16, 2004 after five years of growth (Fig. 3). The new extension of the straw was 20 cm in length, giving a mean annual growth rate of about 4 cm/yr. This rate is very fast compared to other soda straws reported elsewhere (e.g. Baskaran and Iliffe, 1993; Tanahara et al., 1998; Woo et al., 2005). Before sampling, the drip rate was measured five times. Their mean drip rate was about 34 times/day during the summer, but the drip rate per day during winter is almost zero. Seasonal monitoring of temperature, humidity and partial pressure of CO_2 was carried out four times for one year after sampling, and it shows atmospheric conditions at the sample site to be stable (Figs. 2 and 4).

Natural climatic disasters were recorded in the Korean peninsula during the growth period of the SD-1 (Table 1; Fig. 1). The spring of 2000 to that of 2001 was the recorded by Korean Meteorological Administration as the driest season since instrumental meteorological records began in 1904. In September 2002 and September 2003, the Republic of Korea suffered two typhoons, Russa and Maemi that inflicted economic damage of several billion US dollars and left a few tens of thousands of flood victims temporarily homeless.

3. Methods

The fragile soda straw was impregnated by injecting epoxy resin into the central canal before microdrilling powder samples at intervals of 1 cm with a dental drill. A total of 21 microsamples were obtained in this way for geochemical analyses.

$^{210}Pb_{ex}$ (excess or unsupported ^{210}Pb) was analyzed by the method of Woo et al. (2005). To avoid any contamination of ^{210}Pb from cave atmosphere to the surface of the soda straw, the surface of the soda straw was reacted with weak hydrochloric acid and the uppermost surface of the soda straw was mechanically removed before micro-sampling (Tanahara et al., 1998). For ^{210}Pb and ^{226}Ra measurements of the soda straw SD-1, a known amount of the powdered sample was placed in the counting vial and sealed. The sealed samples were left for over 1 month for the daughter products of ^{226}Ra to reach secular equilibrium. For ^{210}Pb and ^{226}Ra, 46.5 keV and 351.9 keV (^{214}Pb) gamma-ray lines were utilized to assay the concentrations of ^{226}Ra and ^{210}Pb. Each sample was counted on HPGe detector for a known amount of time. The counting efficiency curves were obtained using Isotope Products Laboratories multinuclide solution and IAEA gamma-ray reference materials (RGU-1, RGTh-1, and RGK-1) and dpm/cpm ratios for each radionuclide were calculated using IAEA 306 marine coastal sediment (Baltic Sea) reference material. Since the density of samples and reference is very similar, the self-absorption correction was not made (Hasan et al., 2002).

O and C stable isotopes were determined on a VG Isotech Prism II IRMS (Isotope Ratio Mass Spectrometer) at the Korea Basic Science Institute. Analytical error is less than 0.1‰ and δ values are relative to the PDB standard. For trace elemental analysis the samples were dissolved in weak nitric acid and were analyzed on a Thermo Electron CCTED ICP–MS (Inductively Coupled Plasma Mass Spectrometer). Relative standard deviations of the concentrations of analyzed elements for five replicate samples were calculated.

4. Results and discussion

4.1. Rainfall controls on $^{210}Pb_{ex}$ activity concentrations

The massic $^{210}Pb_{ex}$ activity concentrations of the SD-1 display a wide range, from 9.10 ± 3.75 to 88.85 ± 17.57 Bq/g (Table S1 in the Supplementary data). The $^{210}Pb_{ex}$ contents of the SD-1 are higher than the previous data reported from other caves at least by a factor of 10 to 100 (Baskaran and Iliffe, 1993; Tanahara et al., 1998; Paulsen et al., 2003; Woo et al., 2005). The $^{210}Pb_{ex}$ activity concentrations of the SD-1 show significant and consistent seasonal variations (Fig. 3). This result indicates that ^{210}Pb flux was very high during the growth of the soda straw and influx rate varied with seasons.

The ^{210}Pb sources in the soda straw are ^{222}Rn in cave air and drip waters. However, Baskaran and Iliffe (1993) presumed that since the ^{210}Pb concentration in the cave soil (clay layers) is negligible compared to the speleothem concentration, the contribution of ^{210}Pb to speleothems from ^{222}Rn present in the cave air is negligible. Also, if ^{210}Pb contents in the soda straw were controlled only by cave air and ^{222}Rn contents of drip water, it is expected to see nearly constant ^{210}Pb values in the soda straw (Tanahara et al., 1998) and seasonal variations of the SD-1 should not be shown. Therefore, this $^{210}Pb_{ex}$ inventory of the SD-1 cannot be explained only by ^{222}Rn in cave air and drip water, which were considered as potential sources of speleothem $^{210}Pb_{ex}$ in the previous studies.

Another possible source can be found by the $^{210}Pb_{ex}$ was deposited from lower troposphere onto ground surface and soil layers. Noble gaseous, radiogenic ^{222}Rn (half life = 3.82 days) decays into ^{210}Pb (half life = 22.6 years) after emission into the atmosphere from the Earth's surface. Once ^{210}Pb is produced, it may be quickly incorporated into aerosols and subsequently deposited on the surface as dry or wet fallout (e.g., Ioannidou et al., 2005). Migration of atmospherically deposited radionuclides such as ^{210}Pb, ^{137}Cs and $^{239,240}Pu$ in soils and their transfer to groundwater are actively conducted due to preferential flow path and mobile colloid transport (Kersting et al.,