

## Climate fluctuations during the last 3000 years in Guizhou, China: Evidence from the TIMS-U series ages and oxygen isotope composition of stalagmite

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The TIMS-U series ages and the  $\delta^{18}\text{O}$  values of stalagmites from the Qixing Cave, Guizhou (26°4'N, 107°16'E) have been determined using the MAT-262-RPQ and Delta-S mass spectrometers. The results indicate that the stalagmite was deposited during the period of 3145-200 a B.P. and experienced four stages of the climate-environmental change.

(1) The first stage is in the range of 3145-2927 a B.P., which has  $\delta^{18}\text{O}$  values from -5.61 to -5.16‰. This stage corresponds to the late Megathermal Period (7-3 ka B.P.);

(2) The second stage is in the range of 2927-1196 a B.P., which has  $\delta^{18}\text{O}$  values from -5.51 to -4.59‰. Those values are higher than that in the first stage, indicating that the climate has become colder and dryer;

(3) The third stage is in the range of 1196-545 a B.P., which has the  $\delta^{18}\text{O}$  values from -5.98 to -3.92‰. This stage corresponds to the Medieval Warm Period (MWP);

(4) The fourth stage is in the range of 545-200 a B.P., which has the  $\delta^{18}\text{O}$  values from -5.39 to -3.51‰. It had the coldest and driest climate during the period of last 3000 years. This stage corresponds to the Little Ice Age from 1555 A.D. to 1800 A.D.

A regressive equation  $\delta^{18}\text{O} (\text{‰}) = -2.20 \times 10^{-4} \text{ year (a.B.P.)} - 4.54$  by fitting the two data sets of the  $\delta^{18}\text{O}$  values and the age (years). It indicates that the  $\delta^{18}\text{O}$  values become higher from 3145 a B.P. to 200 a B.P. which corresponds to lower precipitation. The warm and wet climate in the late Megathermal Period changed to the cold dry climate in the Little Ice Age. It is interesting to note that on the basis of the climate records during 1951-2000 A.D. measured at the Guiyang Meteorological Observatory (26°35'E, 106°43'N), two regressive equations of the temperature values and the age (years), the precipitation values and the age (years) have the negative slopes, implying that the temperature gradually decreases with an amplitude of -0.2°C and the precipitation gradually decreases with the amplitude of -7 cm during the last 50 years. Thus, the modern climate pattern in Guizhou Province, China, may be continuing from the last 3000 years.

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## Mass-independent sulfur isotopes trace magma-wall rock interactions in the Bushveld Complex

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Abundant metasedimentary xenoliths in the Platreef, the ore horizon of the northern limb of the Bushveld Complex, South Africa, suggest significant interaction between the Bushveld magma and the surrounding country rock during emplacement. Fluid-mediated concentration of Platinum Group Metals and sulfur into the Platreef ore zone likely occurred as a result of this interaction. We use measurements of  $^{33}\text{S}/^{32}\text{S}$  and  $^{34}\text{S}/^{32}\text{S}$  to test hypotheses of material transfer between the Platreef and the surrounding country rock.

Solid-earth fractionation processes of  $^{33}\text{S}/^{32}\text{S}$  and  $^{34}\text{S}/^{32}\text{S}$  are mass-dependent, characterized by:  $\delta^{33}\text{S} \approx 0.515 \times \delta^{34}\text{S}$ . Deviation from mass-dependent isotopic fractionation is quantified as  $\Delta^{33}\text{S} (= \delta^{33}\text{S} - 1000 \times ((1 + \delta^{34}\text{S}/1000)^{0.515} - 1))$ . Proxies for 'primary' igneous sulfur (meteorites, peridotite xenoliths) possess  $\Delta^{33}\text{S}$  values near 0‰. Similarly, relatively pristine Bushveld igneous rocks have  $\Delta^{33}\text{S}$  values  $\leq 0.2$ ‰. On the other hand, sedimentary country rocks surrounding the Platreef exhibit substantial non-zero  $\Delta^{33}\text{S}$  values. As  $\Delta^{33}\text{S}$  is a chemically-conservative tracer, non-zero  $\Delta^{33}\text{S}$  values in Platreef sulfide ore minerals are an indication of material transfer from the surrounding country rock.

We have performed a S isotope study along two profiles through the Platreef into underlying metapelitic and metacarbonate country rocks. In both profiles, far-field igneous rocks have  $\Delta^{33}\text{S}$  values  $\leq 0.2$ ‰, while far-field metasedimentary rocks have significantly mass-independent S isotope compositions ( $\Delta^{33}\text{S}$  ranging up to ~0.9 per mil in the pelitic rocks and up to ~5.0 per mil in the carbonate rocks).

In the metapelitic profile,  $\Delta^{33}\text{S}$  values from the country rocks show only a weak positive correlation with distance from the igneous contact while S isotope compositions within the Platreef are consistent with mass-dependent S isotope compositions ( $\Delta^{33}\text{S} \leq 0.2$ ‰). Both features suggest little magma-wall rock interaction. In the metacarbonate profile, however,  $\Delta^{33}\text{S}$  values in both the country rock and the Platreef define a classic advective-dispersive tracer geometry. This geometry is not present in the associated  $\delta^{34}\text{S}$  values, revealing their susceptibility to post-transport alteration. Displacement of the  $\Delta^{33}\text{S}$  front suggests fluid advection into the country rocks; this was accompanied by back-diffusion of S isotope species into the Platreef. Counterintuitively, then, mineralization may have occurred as a by-product of fluid transport out of the Platreef ore-forming zone.