

On the timing and mechanisms of Heinrich Stadials: a speleothem study from Southern Brazil

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Recent paleoclimate data and modelling results revitalized the debate on the cause of the extreme cold events in the North Atlantic during the last glacial period, the so-called Heinrich Stadials (HS), and their durations. We established a new speleothem $\delta^{18}\text{O}$ record from Botuvera Cave, southern Brazil, with significantly improved data resolution and U/Th chronology. The $\delta^{18}\text{O}$ profiles from multiple stalagmites show that the HS0 (YD), HS2, HS3 and HS4 are about 1,000 years long, centred approximately 12.0, 24.6, 30.0 and 39.0 kyr BP, respectively, whereas HS1 is about 3,000 years long, lasting from 17.5 to 14.5 kyr BP. Following the earlier studies, we interpret the calcite $\delta^{18}\text{O}$ as a proxy of South American Summer Monsoon (SASM) intensity in the region. The abrupt drops on calcite $\delta^{18}\text{O}$ during the HS intervals, with an amplitude of $\sim 2\%$ VPDB, suggest that climate change in this region is manifested as a dramatic increasing of rainfall. The one-to-one correlation with the updated Hulu Cave record confirms our previous finding that on millennial timescales, precipitation change in southern Brazil is anti-phased with that in the north, which is probably controlled by the meridional migration of the intertropical convergence zone (ITCZ). Thanks to micromill sampling techniques and high sample growth rates, we are able to characterize detail precipitation changes in southern Brazil during HS. For example, we did not observe SASM reversals in any HS except HS1 within which a minor $\delta^{18}\text{O}$ jump of $\sim 0.5\%$ can be identified at 15.3 kyr BP. Typically, precipitation increases abruptly in the earlier stage of HS, whereas during the later stage, precipitation decreases more gradually. This asymmetric pattern of change is different from the temperature behavior in the North Atlantic, which warms much more dramatically in the final stage of a HS than it cools in the initial phase. Such decoupling may suggest that ITCZ meridional migration is preferably controlled by the temperature gradient between the high and low latitudes in the cold hemisphere.

Isotope exchange rates and equilibrium fractionation between Cr(III) and Cr(VI)

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Kinetic fractionation of Cr stable isotopes resulting from reduction of mobile and toxic Cr(VI) to immobile and relatively non-toxic Cr(III) has been applied to monitoring and quantifying the extent of reduction in Cr-contaminated groundwater^[1]. However, equilibrium fractionation resulting from isotope exchange between Cr(III) and Cr(VI)^[2], if fast enough, can potentially overprint kinetic isotope fractionations. In this study we measured the exchange rates between solid Cr(III) and dissolved Cr(VI) at 25°C using a ⁵⁰Cr-enriched tracer method. We also measured the equilibrium fractionations between 0.2 M dissolved Cr(III) and 0.2 M dissolved Cr(VI) under acidic conditions at 25°C, 40°C, and 60°C.

At 60°C, the dissolved 0.2M Cr(VI) and Cr(III) reach isotopic equilibrium after ca. 39 days with $\Delta^{53}\text{Cr}_{\text{VI-III}} = 4.9 \pm 0.1 \%$. At 40°C, the system reaches equilibrium at ca. 319 days with $\Delta^{53}\text{Cr}_{\text{VI-III}} = 5.2 \pm 0.1 \%$. At 25 °C, the system evolved only ca. 20% toward equilibrium after 684 days of exchange.

The isotope exchange rates between solid Cr(III) (10 ppm to 100 ppm) and dissolved Cr(VI) (200 μM to 1400 μM) were measured over a range of conditions (pH 6.5 to pH8) and fit to an isotopic exchange model^[3] to obtain the rate law: $R = 5.91 \times 10^{-3} \cdot [\text{Cr(VI)}]^{0.48} \cdot [\text{Cr(III)}]^{0.64} \cdot [\text{H}^+]^{0.39}$, where R gives the isotope exchange rate in mol/L/day. Using this rate law, we estimate that in an aquifer containing 20 μM Cr(VI) and 10 ppm solid Cr(III) with a pH of 7.5, it would take ca. 20 years to evolve halfway toward equilibrium.

Goethite, which we hypothesized might increase the exchange rate as a semi-conductor, actually slowed exchange somewhat, probably due to adsorption of Cr(VI). Anthraquinone-2, 6-disulfonate (AQDS), as an analog of electron shuttle molecules in natural organic matter, accelerated the exchange rate by a factor of 10.

Based on our results, we conclude: 1) higher temperatures, higher concentrations, lower pH, absence of adsorbing agents, and presence of electron shuttles contributed to faster isotope exchange rates between solid Cr(III) and dissolved Cr(VI); 2) For Cr-contaminated aquifers without organic electron shuttles and/or little exposed Cr(III), equilibrium fractionation will not overprint the kinetic-fractionation-based isotope method to monitoring remediation of Cr contamination; 3) For Cr-contaminated aquifers with abundant exposed Cr(III) and dissolved organic electron shuttles present, ⁵³Cr/⁵²Cr ratios of dissolved Cr(VI) may be affected by isotopic exchange over several years time or longer. This would tend to shift the ratios toward equilibrium values and away from values generated by kinetic isotope fractionation occurring during Cr(VI) reduction.

[1] Ellis *et al.* (2002) *Science* **295**, 2060-2062.

[2] Schauble *et al.* (2004) *Chem. Geol.* **205**, 99-114.

[3] Cole *et al.* (2001) *Rev. Mineral. Geochem.* **43**, 83-223.