

## Rainfall induced isotope effects in rice (*Oryza sativa* L.) grain organics: A palaeo perspective

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The relationship between  $\delta^{18}\text{O}$  of environmental water and organic-starch present in rice (*Oryza sativa* L.) and its usefulness to reconstruct precipitation patterns from archaeological samples is being explored in this paper. Rice grows in an environment saturated with water which is derived primarily from rainfall. Being a crop which grows across latitude from tropical to temperate regions, it offers the possibility to explore the relationship that it exhibits with the oxygen isotopic composition of rainfall. Rainfed water is the primary source of water in agricultural fields and is responsible for controlling the growth and productivity of the rice crop. A strong and significant relationship was found to exist between the all-India rice production and Indian summer monsoon rainfall [1]. Here we used  $\delta^{18}\text{O}$  signature of rice grain samples originating from different latitudes, and compared it with the zonal temperature and respective precipitation isotopic ratios. Oxygen isotope ratios in rice grains were obtained from the literature [2, 3] and were also generated upon analysis of samples originating from different locations over India. The isotopic composition of precipitation and temperature were retrieved from International Atomic Energy Agency–Global Network of Isotopes in Precipitation (IAEA – GNIP) dataset [4]. A careful inspection of precipitation isotope ratios and rice isotopic composition, allowed the determination of  $\delta^{18}\text{O}$  fractionation factor between rice organics and precipitation water. The fractionation factor observed in here varies between ~23‰ to ~35‰ and is mainly controlled by temperature. The latitudinal effect on rice isotopic composition and rainfall is observed in majority of the locations. However, the regions affected by dual monsoon show tendency of large scatter owing to contribution of moisture from different ocean basins [5]. The oxygen isotope ratios in rice samples will provide an opportunity to understand the rainfall pattern from isotopic composition of rice samples belonging to archaeological sites of older civilizations.

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## Stable-isotope insights into mineral-fluid redox reactions

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We present a synthesis of a series of experiments which use metal stable isotope behavior as a probe of the kinetics of redox reactions at an aqueous/solid interface. Measurements of isotope fractionation during potentiostat-controlled electroplating has led to observations of large isotope fractionation factors in a large variety of metal systems including Fe [1-3], Zn [2-5], Li [6], and Cu[7]. Our observed isotope fractionations vary strongly as a function of electrochemical driving force and temperature. We interpret our observations in terms of a competition between two rate-limiting steps at a redox-sensitive interface: mass transport to the interface, which results in small isotope signatures, and the steps associated with the electron transfer reaction, which results in much larger isotope signatures. Our experimental data which measures both overall reaction rates and rate-dependent isotope separation cannot be explained simultaneously using rate laws involving simple single-step activated processes governing mass transport and redox reaction steps. Instead, to explain all of our observations, we require rate-dependent isotope fractionation factors. Our results are consistent with a theory predicting isotope-dependent electrochemical reaction rates that is based on theory for electron transfer reactions[1,4]. The results imply that stable isotope behavior at a redox-active interface provides an exquisitely sensitive probe of the details of the activated processes governing the reactions, elucidating small variations in rate that cannot be observed by measuring reaction rates alone. This is especially true in regimes where redox processes are not rate-limited by mass transport of material to the reaction zone.

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