Impact of seasonally variable soil carbonate formation on paleotemperature records from clumped isotopes

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Reconstructing environmental temperatures from the continental geologic record is important for investigating the evolution of life, climate, tectonics, and landforms, yet direct temperature estimates are difficult to obtain from conventional isotopic and paleobotanical proxies. Measurement of 'clumped' ^{13}C-^{18}O bonds in calcium carbonate provides independent estimates of the formation temperature, $\delta^{13}C$ value, and $\delta^{18}O$ value of the carbonate and enables calculation of the $\delta^{18}O$ value of the water from which the mineral grew--each of which can provide important paleoenvironmental constraints. When applied to pedogenic carbonates, clumped isotope thermometry can quantify Earth surface paleotemperature and the $\delta^{18}O$ value of ancient surface waters, from which changes in climate or surface elevation might be inferred. However, recent studies suggest a strong seasonal bias in soil carbonate growth, complicating the interpretation of both temperature and $\delta^{18}O$ data from paleosols.

We use clumped isotope thermometry of recent soil carbonates and monitoring of local weather and soil subsurface conditions to investigate how seasonal variations in environmental factors such as soil temperature, precipitation, and vegetation influence rates of soil carbonate formation. Pedogenic carbonate samples formed in Holocene to Recent soils were collected from soil pits along a transect spanning 2 km of relief in the southern Central Andes of Argentina (33°S) with high seasonal variations in precipitation, air temperature, and soil temperature.

Because soil carbonate formation is generally favored in warm, dry conditions, we expected carbonate growth temperatures from clumped isotope thermometry to exceed mean annual soil temperatures at the sample sites. Instead, we find clumped isotope temperatures vary significantly between mean annual and and greater than mean annual soil temperatures. Samples below 2000 m elevation (where winters are dry) record temperatures from 0 to 4.5°C above mean annual soil temperature, while samples above 2000 m (where summers are dry) are >5.5°C above mean annual soil temperature, suggesting the influence of seasonal variations in both temperature and precipitation. For some sites, clumped isotope temperatures for samples at depths >50 cm in the soil profile exceed maximum soil temperatures measured over the period of record, likely reflecting enhanced carbonate formation during warm periods over the last 10^2-10^3 years. Temperatures for these deeper samples also exceed temperatures for samples near the surface, suggesting that sampling paleosols deep in the soil profile, a practice designed to avoid large temperature bias, could actually introduce greater biases in soil temperature estimates used to interpret conventional $\delta^{18}O$ data.

The effect of different metal species on the evolution with pressure of hydration clusters in water vapour

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The hypothesis that transport of metals by vapour is a viable mechanism for ore formation in magmatic-hydrothermal systems is supported by fluid inclusion data and the occurrence of metal-rich incrustations around fumaroles. A feature of this hypothesis is that hydration of metal species in water vapour is an essential factor in making such transport possible [1,2]. Indeed, hydration has been shown to increase concentrations of Ag and Au in the gas phase by several orders of magnitude over those calculated using volatility data. Nevertheless metal concentrations determined experimentally are substantially lower than those reported for vapour inclusions in magmatic hydrothermal systems.

We have shown previously that hydration numbers are not constant but increase exponentially with increasing water pressure. As a result, metal solubility increases by orders of magnitude from its values at low pressure to those at conditions approaching saturation of the vapour with liquid. In the current study, we are building on this earlier work by conducting experiments designed to determine the effect of different metallic vapour species on the nature of the surrounding hydration cluster with changing P_{H_2O}.

The experiments were conducted in batch-type Ti autoclaves at a constant oxygen fugacity, buffered by the assemblage MoO_2-MoO_3. From comparison of the experimental data sets for $AuCl(H_2O)_n$ and $MoO_3(H_2O)_n$, it is apparent that the solubility of these two species is described by different exponential functions. The solubility of the Au-chloride species is, within experimental error, independent of pressure below 87 bars P_{H_2O} and increases with increasing pressure to a value three log units higher at conditions approaching saturation of the vapour with liquid. By contrast, the solubility of the Mo-oxide species is only observed to increase above 150 bars P_{H_2O}, and at conditions approaching saturation, is only 1.5 log units higher than at pressures below 150 bars P_{H_2O}. This likely indicates that the molecular structure or the type of bonding of the metal species has an important control on the nature and size of the hydration clusters.

Experiments performed at conditions of saturation, i.e., with vapour and liquid present, indicate that there is a continuum between metal solubility in the vapour and that in the corresponding liquid. Above the critical point, the form of the hydration curve does not change significantly, indicating the formation of stable hydration clusters under these conditions and a continuous increase in solubility with increasing P_{H_2O} from vapour-like to liquid-like supercritical fluids.

[1] Migdisov et al. (1999) *Geochim. Cosmochim. Acta* **63**, 3817
[2] Archibald et al. (2001) *Geochim. Cosmochim. Acta* **65**, 4413