

## **S cycling and capture: Robust records in speleothems, trees and Snowball lakes**

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Terrestrial archives are good for yielding data on atmospheric properties. The versatility of S archives in characterizing environment and climate is illustrated by three contrasting examples. CAS (carbonate-associated sulphate) in some alpine speleothems can give records of atmospheric pollution. S abundance primarily reflects the flux of soil-mediated sulphate into the underlying karst, but lags the peak pollution input by around 20 years. S isotope ratios reflect the pollution contribution. Atmospheric sulphate is assimilated in different forms into organic matter and re-oxidized giving rise to a characteristic new sulphate  $^{18}\text{O}$  composition. Annual variability of S incorporation can be related to the changing pH of the cave environment reflecting temperature-controlled seasonal changes in air circulation. In theory, the structure of the annual S distribution should reflect the relative length of the winter and summer seasons. S distributions in conifer wood have been studied from close to a cave site in northern Italy where a speleothem S record had already been obtained. S is structurally assimilated in the inner cell wall where it is present in a consistent mixture of various oxidation states from 0 to +6. The time distribution of S, like that of speleothems, is a lagged response to atmospheric pollution. Scatter of data indicates that multiple profiles are needed for accurate environmental characterization, as is normal in study of other dendroclimatological properties. CAS records from a lacustrine carbonates in a Neoproterozoic glacial succession from Svalbard revealed a facies-specific distribution of  $^{17}\text{O}$  anomalies and  $^{18}\text{O}$  compositions. Preservation of a  $^{17}\text{O}$ -disturbed atmosphere (probably very  $\text{CO}_2$ -rich) atmosphere in less saline facies is erased by redox cycling in  $^{18}\text{O}$ -rich hypersaline facies.

## **Noble gas and halogen evidence for the origin of mineralising fluids in orogenic gold deposits: An example from the Ballarat East Deposit, Australia**

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The Ballarat East gold deposit (408t) is the second largest turbidite-hosted orogenic gold deposit (after Bendigo) in the western Lachlan Fold Belt, southeast Australia. Gold mineralisation is intimately associated with pyrite, sphalerite and galena, with gangue minerals including quartz, carbonate and white mica. Episodic gold mineralisation between 450 and 375 Ma ( $^{40}\text{Ar}/^{39}\text{Ar}$  ages) suggests long-lived hydrothermal activity. The  $\text{H}_2\text{O}-\text{CO}_2$  fluids responsible for mineralisation have not been investigated in detail previously, but are suggested to have been evolved from devolatilising metavolcanics during Lachlan Fold Belt orogenesis (ca. 440 Ma).

Gold-bearing quartz veins from the Ballarat East deposit contain low salinity (av. 5 wt% NaCl eq.)  $\text{H}_2\text{O}$  inclusions and mixed  $\text{H}_2\text{O}-\text{CO}_2$  fluid inclusions. The noble gas isotope ( $^{40}\text{Ar}$ ,  $^{36}\text{Ar}$ ,  $^{84}\text{Kr}$  and  $^{129}\text{Xe}$ ) and halogen (Cl, Br and I) composition of these fluid inclusions was determined simultaneously by noble-gas mass spectrometry of irradiated quartz samples (extended Ar-Ar methodology). The noble gases and halogens provide powerful constraints on the origin and interaction of fluids. The noble gases have isotopic compositions that vary by orders of magnitude between the hydrosphere, crust and mantle, and the halogens provide the only direct constraint on the fluids acquisition of salinity.

Fluid inclusion  $^{40}\text{Ar}/^{36}\text{Ar}$  values range from  $316 \pm 3$  (close to Air Saturated Water;  $\sim 296$ ) up to a maximum of  $3101 \pm 155$ , and  $^{40}\text{Ar}/^{36}\text{Ar}$  is strongly correlated with  $\text{Cl}/^{36}\text{Ar}$ . Fluid inclusions have variable Br/Cl values between  $1.6 \times 10^{-3}$  and  $2.83 \times 10^{-3}$  and I/Cl values between  $237 \times 10^{-6}$  and  $485 \times 10^{-6}$ , with a strong correlation between Br/Cl and I/Cl. The fluid inclusion  $^{84}\text{Kr}/^{36}\text{Ar}$  and  $^{129}\text{Xe}/^{36}\text{Ar}$  values are also variable and correlated. The data strongly favour the involvement of two fluid end-members: i) the lowest  $^{40}\text{Ar}/^{36}\text{Ar}$  values are consistent with surficial fluids and/or sedimentary formation waters with the highest I/Cl values favouring fluid interaction with organic-rich shales; and ii) the products of local metamorphic devolatilisation and/or magmatic fluids. Further work incorporating Ne isotopes is underway to test if the higher  $^{40}\text{Ar}/^{36}\text{Ar}$  fluid (minimum value of  $\sim 3100$ ) is related to metamorphism or magmatism.