

## Deep Earth volatile cycles: From ancient to modern

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Earth's mantle is significant reservoir for key volatile species and exchange between the mantle and near-surface reservoirs (=“exosphere”) influences planetary climate and habitability as well as dynamical evolution of the interior. Volatile cycling is governed in large part through plate tectonic processes but also has significant influence on regulating the vigour of plate tectonics. Yet, it is not clear how this coupling between geodynamical and geochemical evolution arose or whether one was a prerequisite for the establishment of the other. Originally, much of Earth's volatile inventory was presumably present as a thick atmosphere, in part because volatiles were probably delivered late in the accretion history and because of the efficiency of impact degassing. The early inventory of mantle H<sub>2</sub>O may descend from the magma ocean, in which portions of a steam atmosphere are dissolved in the magma and then precipitated with nominally anhydrous minerals. In contrast, low magmatic solubility of C-bearing species may suggest that the earliest mantle was depleted in C. Thus, the earliest Earth could have been characterized by an exosphere with low H/C and a mantle with high H/C – the reverse of the modern case in which the mantle has low H/C (as demonstrated by H/C ratios of minimally degassed oceanic basalts) and the exosphere high H/C. Thus, either some process retained carbon in the early mantle or subsequent evolution has preferentially sequestered carbon in the interior.

In this plenary review, I will consider the current state of the principal reservoirs of H and C and explore the possible key influence of magma ocean processes on the subsequent evolution of Earth's volatile cycling.

## Re-Os dating and trace element characteristics of pyrite from the Lisheen Pb-Zn deposit, Ireland

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The Lisheen Mine in the Irish Midlands exploits a typical example of a carbonate-hosted base metal deposit from the district. Like the majority of the Irish Pb-Zn deposits, Lisheen is hosted by Lower Carboniferous strata, but the timing of sulfide mineralization is only poorly constrained by geochronologic methods. As such, the genetic models for this important type of sedimentary-hosted ore remain controversial, with timing constraints provided primarily by geologic relationships and, more recently, by paleomagnetic data. The widely proposed syngenetic and syndiagenetic models require that mineralization occurred around the stratigraphic age of ca. 345 Ma, but none of the available geochronological constraints gives this age. Recent paleomagnetic data from Lisheen has been interpreted to indicate post-Variscan epigenetic mineralization at ~277 Ma, much younger than previously proposed and in apparent contradiction to Variscan (~300 Ma) thrust deformation of the ores. In order to address this problem we have applied Re-Os dating to main ore-stage pyrite from different parts of the deposit. Pyrite samples from the Main Zone, Derryville Zone, and Bog Zone were found to be very variable in Re/Os ratios (300 – 10000), as well as in the trace element abundances in general. Thirty-three Re-Os analyses of pyrite from the Main Zone, Bog Zone, and the nearby Galmoy deposit yielded an age of 342 ± 5 Ma, within uncertainty of the stratigraphic age. However, data from the Derryville zone give an age of 306 ± 10 Ma with a very high initial <sup>187</sup>Os/<sup>188</sup>Os value of 3.6, suggesting resetting. The variation within and between these isochrons were investigated using electron microprobe and ICPMS analysis to help understand the relationship between rhenium, various trace elements, pyrite morphology and its subsequent alteration. Based on our results it is evident that pyrite throughout Lisheen has been heavily disturbed providing a possible explanation for the scatter seen in the isochrons and a reason why the paleomagnetic age of 277 Ma does not appear to record the timing of primary sulfide mineralization.