

Study of candidate matrix-matched calibration standards for geological applications by nuclear and laser ablation based methods

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Laser ablation with induction coupled mass spectroscopy (LAICPMS) and laser induced breakdown spectroscopy (LIBS) became widely used in geological sciences. For quantification procedure of methods based on laser ablation, the matrix matched standards are required. Such standards, are largely lacking, especially for geological applications. We aimed at filling this gap by analyzing minerals, rocks, fused powdered rocks, sol-gel derived and plasmochemically deposited mineral analogues to identify possible candidate materials. The homogeneity and trace elements contents of the above mentioned materials were examined using μ -PIXE, LAICPMS-screening and by PIXE/PIGE/INAA techniques. Major/minor elements were studied using EPMA. PIGE is capable to detect some light elements that are not detectable by X-ray spectroscopic methods. INAA provides reliable informations about trace element composition of examined materials, with favourable detection limits compared with the majority of common analytical techniques.

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Constraints on Earth outgassing history from Ar isotope composition of Devonian atmosphere

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The noble gases have long been used to show that the terrestrial atmosphere resulted from the outgassing of the Earth's interior rather than capture of the solar nebula during accretion. The primordial and radiogenic isotopes of the noble gases combine to make them a powerful tool for determining the time and tempo of Earth outgassing. Our understanding of the outgassing history of the Earth is largely derived from measurements of He, Ne, Ar and Xe isotope in samples of modern mantle, crust and atmosphere. Despite several attempts [1] there has been no unequivocal measurement of the isotopic composition of noble gases in ancient atmosphere.

We have now determined the Ar isotope composition of pristine samples of the 404 Ma Rhynie chert using a new multi-collector mass spectrometer and a low blank laser extraction technique. $^{40}\text{Ar}/^{36}\text{Ar}$ are systematically lower than the modern air value, and are not accompanied by non-atmospheric $^{38}\text{Ar}/^{36}\text{Ar}$ ratios. We conclude that the Rhynie chert has captured Devonian atmosphere-derived Ar. The data indicate that the $^{40}\text{Ar}/^{36}\text{Ar}$ of Devonian atmosphere was at least 3 % lower than the modern air value. Thus the Earth's atmosphere has accumulated at least $5 \pm 0.2 \times 10^{16}$ moles of ^{40}Ar in the last 400 million years, at an average rate of $1.24 \pm 0.06 \times 10^8$ mol $^{40}\text{Ar}/\text{year}$. This overlaps the rate determined from ice cores for the last 800,000 years [2] and implies that there has been no resolvable temporal change in outgassing rate since the mid-Palaeozoic. The new data require outgassing early in Earth history, and suggest that pristine samples of Archaean and Proterozoic chert may prove useful as palaeo-atmosphere tracer.

[1] Turner, G. (1989) *J. Geol. Soc. London* **146**, 147–154.

[2] Bender, M. *et al.* (2008) *Proc. Nat. Acad. Sci.* **105**, 8232–8237.