

## Unleashing the full potential of the $^{40}\text{Ar}/^{39}\text{Ar}$ geochronometer

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$^{40}\text{Ar}/^{39}\text{Ar}$  geochronology has long suffered from large systematic errors arising from imprecise K and Ar isotopic data for standards and imprecisely determined decay constants for the branched decay of  $^{40}\text{K}$  by electron capture and  $\beta^-$  emission. This study presents a statistical optimization approach to improving the situation, using constraints from  $^{40}\text{K}$  activity data, K-Ar isotopic data, and 16 pairs of  $^{238}\text{U}$ - $^{206}\text{Pb}$  zircon and  $^{40}\text{Ar}/^{39}\text{Ar}$  data for rigorously selected volcanic rocks as inputs for estimating the partial decay constants ( $\lambda$  and  $\lambda_e$ ) of  $^{40}\text{K}$  and the  $^{40}\text{Ar}/^{40}\text{K}$  ratio ( $K$ ) of the widely used Fish Canyon sanidine (FCs) standard. The  $^{238}\text{U}$ - $^{206}\text{Pb}$  ages were corrected for  $90 \pm 77$  ka mean pre-eruptive residence time (Simon *et al.* 2008). The optimized results yield values of  $K = (1.6418 \pm 0.0046) \times 10^{-3}$ ,  $\lambda_e = (0.5755 \pm 0.0016) \times 10^{-10}/\text{a}$  and  $\lambda_e = (4.9737 \pm 0.0092) \times 10^{-10}/\text{a}$ ; all uncertainties stated at one sigma. These results improve uncertainties in the decay constants by a factor of  $>5$  relative to values derived from activity data alone. Uncertainties in these variables determined by our approach are highly correlated and error propagation must include their covariances [ $\text{cov}(K, \lambda_e) = 7.3620 \times 10^{-19}$ ,  $\text{cov}(K, \lambda_e) = -6.8299 \times 10^{-19}$ ,  $\text{cov}(\lambda_e, \lambda_e) = -3.4811 \times 10^{-26}$ ] or use Monte Carlo-type simulations. Age errors estimated from these results are significantly improved relative to previous calibrations, i. e., producing smaller age errors than the astronomical calibration of Kuiper *et al.* (2008) for ages  $>6$  Ma, up to a factor of 10 smaller than the latter at 4.5 Ga. The age we derive for FCs is  $28.305 \pm 0.031$  Ma. Age errors are smaller for a comparable level of analytical precision in isotope measurement data than those produced by the  $^{238}\text{U}/^{206}\text{Pb}$  system. Thus ironically, despite being partly calibrated by it, the  $^{40}\text{Ar}/^{39}\text{Ar}$  system is now capable of accuracy comparable to and even exceeding that of the  $^{238}\text{U}/^{206}\text{Pb}$  'gold standard' in certain circumstances. A case in point is the Permo-Triassic boundary, whose new  $^{40}\text{Ar}/^{39}\text{Ar}$  age (recalculated from Renne *et al.* 1995) is  $252.27 \pm 0.08$  Ma, compared with a  $^{238}\text{U}/^{206}\text{Pb}$  age of  $252.40 \pm 0.33$  Ma (Mundil *et al.* 2004), including systematic errors in both.

## First principles investigation of coupled substitution in Galena

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Coupled substitution is an important mechanism responsible for Ag enrichment in galena. Studies show that the concentration of Ag in galena will tend to equal the sum of the concentrations of Sb and Bi [1]. The thermodynamic mixing properties of the binaries  $\text{Pb}_2\text{S}_2\text{-AgSbS}_2$ ,  $\text{Pb}_2\text{S}_2\text{-AgBiS}_2$ , and  $\text{Pb}_2\text{S}_2\text{-AgAsS}_2$  have been investigated using first-principles and Monte-Carlo calculations similar to the method used by Reich *et al.* [2]. Quantum mechanical methods were used to account for electron transfer between the substituting species. Total energies for different substitution configurations were used in Monte-Carlo calculations to derive the excess enthalpy of mixing ( $\Delta H_{\text{excess}}$ ), entropy of mixing ( $\Delta S_{\text{excess}}$ ), and free energy of mixing ( $\Delta G_{\text{excess}}$ ) at temperatures ranging from 200 °C to 700 °C.  $\Delta G_{\text{excess}}$  was used to calculate phase diagrams that can be compared with experiment. Miscibility gaps dominate the  $\text{Pb}_2\text{S}_2\text{-AgSbS}_2$  and  $\text{Pb}_2\text{S}_2\text{-AgAsS}_2$  binaries for  $X_{\text{Ag}} < 0.25$ , whereas  $\text{Pb}_2\text{S}_2\text{-AgBiS}_2$  has a complete solid solution at temperatures  $>200^\circ\text{C}$ , in rough agreement with experiments [3]. Electron transfer between Ag and either Sb, Bi, or As is shown to affect cation-ordering in these systems. Quantum mechanical simulations allow for visualization of specific orbitals that are predominantly responsible for this electron transfer. Intermediates of the  $\text{Pb}_2\text{S}_2\text{-AgBiS}_2$  solid solution tend to order into alternating Ag-rich layers parallel to  $\{111\}$  and Pb/Sb-rich layers.

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