

## $^{16}\text{O}^1\text{H}$ signal as an indication of metamict O-contamination in zircon

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Although zircons are generally considered to be refractory with respect to oxygen isotope signatures, metamiction can make the mineral susceptible to O-isotope exchange. A variety of means are available to indicate metamict conditions, i.e. electron microscopy, common Pb contamination, Raman spectroscopy,  $\alpha$ -damage etc., however, these methods may be inconvenient or may in some cases lead to the erroneous conclusion that the zircon is pristine. We introduce here a SIMS based technique that can provide evidence of metamiction and at the same time perform  $\delta^{18}\text{O}$  analyses—namely the analysis of the  $^{16}\text{O}^1\text{H}$  signal. The technique is particularly well suited to multicollector instruments and can be utilized with little to no decrease in  $\delta^{18}\text{O}$  precision. In a pilot study using the technique, we found that elevated  $^{16}\text{O}^1\text{H}/^{16}\text{O}$  relative to a highly crystalline standard (CZ3;  $^{16}\text{O}^1\text{H}/^{16}\text{O} = 0.00136 \pm 0.00006$ ; mean  $\pm 1$  SD) was correlated with apparent radiation damage and we interpret an increase in this signal to indicate excess  $\text{H}_2\text{O}$  in the mineral. Although  $\delta^{18}\text{O}$  in these amorphous regions varied from  $-7\text{‰}$  to  $+8.5\text{‰}$  (VSMOW; Fig. 1), regions with  $^{16}\text{O}^1\text{H}/^{16}\text{O}$  values less than 6 SD above the CZ3 mean value were all interpretable as mantle  $\delta^{18}\text{O}$  values. We found that the magnitude of the  $^{16}\text{O}^1\text{H}/^{16}\text{O}$  on pristine zircons is dependant upon chamber vacuum and sample degassing and it is unclear if the zircon signal is detectable above background. However, at a given vacuum, four different standards gave statistically indistinguishable  $^{16}\text{O}^1\text{H}/^{16}\text{O}$  values.

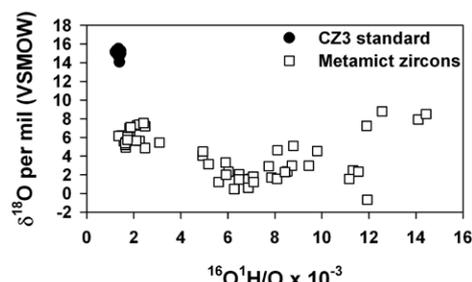


Fig 1. Comparison of  $\delta^{18}\text{O}$  and  $^{16}\text{O}^1\text{H}/\text{O}$  in the CZ3 standard and metamict zircons.

## Doubly $^{13}\text{C}$ -substituted ethane

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Most natural gas reservoirs contain significant amounts of ethane ( $\text{C}_2\text{H}_6$ ). Here we examine the geochemistry of multiple  $^{13}\text{C}$  substitutions in this molecule. Several processes can plausibly influence the abundances of  $^{13}\text{C}_2\text{H}_6$  in natural gases: inheritance from larger biomolecules in source rocks; kinetic fractionations associated with thermal degradation or organic matter; isotope exchange reactions at thermodynamic equilibrium; and/or mixing of gases with different bulk isotopic composition. There is little basis for a priori predictions as to which of these processes will dominate in nature. We present the mass spectrometric techniques for measurement of  $^{13}\text{C}_2\text{H}_6$  at natural abundances, using a high-resolution gas source isotope ratio mass spectrometer (the Thermo 253 Ultra), and explore the chemistry of this species through experiments and initial results on conventional thermogenic natural gases.

The high resolutions of the Ultra (up to 27,000,  $M/\Delta M$ ) allow clean separation of obvious interferences (e.g.,  $\text{O}_2$  or  $\text{CH}_3\text{OH}$  at  $m/z=32$ ). Most critically, we are able to discriminate the doubly-substituted isotopologues  $^{13}\text{C}_2\text{H}_6$  from  $^{13}\text{C}^{12}\text{CDH}_5$  at  $m/z=32$ . However, we find it is fastest and most precise if we analyse the sum of both singly-substituted isotopologues at  $m/z=31$ ,  $^{13}\text{C}^{12}\text{CH}_6$  and  $^{12}\text{C}_2\text{H}_5\text{D}$ , and then calculate  $\delta^{13}\text{C}$  based on a conventional measurement of  $\delta\text{D}$ . We report abundances of  $^{13}\text{C}_2\text{H}_6$  as an enrichment relative to a stochastic reference frame:  $\Delta^{13}\text{C}_2\text{H}_6 = 1000 * ((^{13}\text{C}_2\text{H}_6 / \text{C}_2\text{H}_6) / (^{13}\text{C}_2\text{H}_6 / \text{C}_2\text{H}_6)_{\text{stochastic}} - 1)$ .

Measurements of the  $^{13}\text{C}_2\text{H}_6 / ^{12}\text{C}_2\text{H}_6$  ratio are limited by counting statistics down to  $\pm 0.15$  per mil (1 s.e.). The corresponding precision in  $\Delta^{13}\text{C}_2\text{H}_6$  is  $\pm 0.2$  per mil (1 s.e.), when one includes the small additional uncertainties in the 31/30 ratio and conventional  $\delta\text{D}$  measurements. Replicate extractions of natural samples are reproducible to better than  $\pm 0.5 \text{‰}$ . Analyses of synthetic gas mixtures confirm that fragmentation/ recombination reactions in the ion source are not a major factor. Preliminary work on ethane from thermogenic gases showed a total range in  $\Delta^{13}\text{C}_2\text{H}_6$  of 4 ‰. The expected range in  $\Delta^{13}\text{C}_2\text{H}_6$  due to thermodynamic equilibrium alone at typical temperatures of natural gas generation and storage is only  $\sim 0.2\text{--}0.3 \text{‰}$ . Thus, our results suggest that proportions of  $^{13}\text{C}_2\text{H}_6$  in natural gases are largely controlled by inheritance from organic precursors and/or kinetic isotope effects associated with gas generation. This is an expected result because isotopic exchange of the C-C bond in ethane is likely slow under geological conditions.