# High spatial resolution measurements of $\delta^{18}$ O in authigenic quartz overgrowths

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# Introduction

Authigenic quartz cements commonly account for as much as 50% of the loss of porosity in sandstones and as such, represent the major source of porosity occlusion and loss of reservoir capacity in oil and gas fields. The source of silica, its transport mechanism and cause of quartz precipitation however remain essentially unknown. A lively debate centres on whether aqueous pore fluids are of surface, meteoric origin or of deep basinal origin, over what distances the silica is carried in solution and whether the precipitation that results from mixing of pore waters or sandstone-pore water interaction is continuous or episodic. The lack of consensus on such fundamental parameters clearly limits any reliable modelling of the geological systems in which quartz diagenesis occurs.

## Method.

Authigenic quartz can be distinguished from detrital quartz grains by cathodoluminescence, multi-generation growth zones being readily apparent. However, the chemical purity and small spatial scale (typically less than 100µm) of authigenic quartz, make any form of analysis extremely difficult. The only parameter which may be used to determine the source fluids is  $\delta^{18}$ O and attempts have been made to separate overgrowths from detrital grains using various mechanical and chemical segregation techniques. Contamination from detrital grains has proved almost impossible to avoid, making conclusions tenuous and unreliable.

Oxygen isotope analysis by ion microprobe has potentially the spatial resolution and precision required to analyse such small samples, but historically reproducible ion probe measurements have proved elusive. This is due to the large natural abundance differences between the oxygen isotopes  $({}^{16}O/{}^{17}O = 2650, {}^{16}O/{}^{18}O = 500)$  which

places a severe strain on the dynamic range of single collector instruments; reliable charge compensation to neutralise charging in insulating mineral samples and variable instrumental isotopic fractionation which can make measured ratios vary, often by up to 10s of permil. We have made extensive studies of these problems and developed techniques which allow the acquisition of reproducible  ${}^{17}\text{O}/{}^{16}\text{O}$  and  ${}^{18}\text{O}/{}^{16}\text{O}$  ratios in natural mineral standards. (1 $\sigma < 1\%$  in  ${}^{18}\text{O}/{}^{16}\text{O}$  over many different spots on a sample in short time scales, < 30 minutes per spot).

We have used an Isolab 54 ion microprobe (Fisons Instruments) which uses multicollection of different isotopes to overcome problems of dynamic range (<sup>16</sup>O collected by a Faraday detector, <sup>17</sup>O and <sup>18</sup>O measured by a new type of ion detector, a channeltron with a conversion dynode (CDS) which has an extremely uniform, stable and high ion to pulse conversion efficiency). We use a high energy electron gun to effect charge neutralisation of the measured spot. Additionally we have developed a technique for sweeping the secondary ion beam at high frequency across the source slit of the mass spectrometer thus integrating and eliminating most instrumental fractionation effects. The elimination of most instrumental fractionation coupled with the very high gain stability of the CDS detectors has resulted in high reproducibility of oxygen isotope ratio measurements.

## Results

Measurements of  $\delta^{18}$ O values for a range of quartz standards (natural and synthetic) made over several days show extremely good correlation between our ion probe determinations and conventional (fluorination) values, giving us confidence in our ability to make reliable  $\delta^{18}$ O measurements. We have applied this technique to acquire  $\delta^{18}$ O profiles across a detrital grain and its enclosing authigenic quartz overgrowth from the Piper Formation Sandstone, a major oil-bearing reservoir sandstone from the Outer Moray Firth of the Central North Sea. This sandstone contains up to 25% bulk sandstone volume authigenic quartz. Cathodoluminescence reveals two growth generations, both of which contain fluid inclusions. Homogenisation temperatures of these fluid inclusions in the sample investigated with the ion probe range between 95°C and 108°C.

 $\delta^{18}$ O values were calibrated against a quartz standard designated seed quartz ( $\delta^{18}O_{SMOW} =$ -4.78‰) and yielded consistent  $\delta^{18}$ O values on the detrital grain of +14.0‰ +1.1‰ (SMOW). With the exception of two spots which have probably been contaminated by sampling a large fluid inclusion, all spots in three profiles on the quartz overgrowth gave consistent values of +23.3‰ ± 1.1‰ (SMOW). All errors are 1 $\sigma$  and also include the error from the scatter of measurements on the seed quartz standard.

The temperature evolution across the overgrowth recorded from fluid inclusion homogenisation temperatures should result in a variation of 1.7% between the centre and edge of the overgrowth. However, within error, the  $\delta^{18}O$  across the overgrowth is constant and implies another process has influenced the  $\delta^{18}O$  composition of the overgrowth. We speculate that either the  $\delta^{18}O$  composition of the pore fluid from which the overgrowths precipitated evolved during quartz precipitation independent of the precipitation mechanism or that the quartz overgrowth  $\delta^{18}O$  has reset at higher burial temperatures subsequent to quartz precipitation.

# References

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