

Ion probe oxygen isotope analysis of quartz and magnetite from the Biwabik Iron Formation, Minnesota

S. J. Cornah
I. C. Lyon
C. D. Curtis

Department of Earth Sciences, University of Manchester, Oxford
Road, Manchester M13 9PL, UK

J. M. Saxton
K. G. Taylor

Department of Environmental and Geographical Sciences,
Manchester Metropolitan University, Chester Street, Manchester,
M1 5GD, UK

The oxygen isotopic compositions of coexisting quartz and magnetite have previously been measured, using conventional fluorination techniques, in samples from a number of Precambrian iron formations (e.g. Perry and Bonnischen, 1966; Perry *et al.*, 1973). Their aim was to utilize equilibrium mineral pair geothermometry to infer temperatures of metamorphism and diagenesis of both recrystallized and relatively unaltered Precambrian chemical sediments. The present study has acquired *in situ*, high spatial resolution, ion probe oxygen isotope measurements of samples from the relatively undeformed Biwabik Iron Formation, Minnesota, in conjunction with detailed petrographic observation. This had the aim of testing the extent of isotopic equilibrium between this mineral pair to investigate the interplay of depositional signatures and modifications due to diagenetic recrystallization of initial precipitates.

Methods. Detailed petrographic observation and compositional analyses were obtained of seven samples from cores 2, 5 and 7 from the Biwabik Iron Formation of the Mesabi Deep Drilling Project (details in Pfeider *et al.*, 1968). Oxygen isotope analyses of these samples were then obtained using the Isolab 54 ion microprobe at the University of Manchester, UK (Saxton *et al.*, 1996). The $^{18}\text{O}/^{16}\text{O}$ ratios were determined by secondary ionization mass spectrometry using a Cs^+ primary beam and the $\delta^{18}\text{O}_{\text{SMOW}}$ values determined by calibration with standard materials (Lyon *et al.*, 1995). Analysis transects of between 11 and 19 spots were made across quartz and magnetite in the selected areas within the chosen samples with crater sizes ranging from 20 to 60 μm in diameter and a few μm in depth.

Results and discussion. Petrographic observation at high resolution identified magnetite as a late stage mineral, generally with a subhedral to euhedral

crystal habit from 10 to 100 μm , which exhibited a cross-cutting relationship with all the other constituent phases. It was present in a number of textural associations including granule rims, replaced granules, disseminated crystals and crystalline aggregates. Quartz was present as a microcrystalline matrix mineral between the disseminated and aggregated magnetite crystals.

Mean values for quartz and magnetite within each sample were calculated to enable the determination of the oxygen isotopic fractionation (ΔQM) between this coexisting mineral pair. These values are shown in Table 1. Mean quartz values range from 18.3 to 24.2 ‰ and mean magnetite values range from -10.7 to -3.6 ‰. The calculated isotopic fractionations range from 25.6 to 33.6 ‰.

Our data have been plotted in Fig. 1 in conjunction with previously published oxygen isotope analyses of the quartz-magnetite mineral pair from the Biwabik Iron Formation (Perry and Bonnischen, 1966; Perry *et al.*, 1973).

Oxygen isotope ratios of quartz and magnetite from the metamorphosed Duluth contact zone and the transition zone between this and the relatively undeformed iron formation are shown by open circles (Perry and Bonnischen, 1966). Data from samples taken from the same cores as the present study (Perry *et al.*, 1973) are plotted as solid diamonds and lie in a steeply dipping array towards lower quartz and higher magnetite values than the present results. An average fractionation of 24‰ was determined from this data. This is almost 10‰ lower than the highest fractionation shown by the present study (open diamonds). This can be explained by a comparison of ion microprobe analysis and the conventional fluorination techniques that were used to generate the other data sets. Firstly, ion probe analysis eliminates the effects of contamination of

TABLE 1. Mean oxygen isotope compositions of quartz and magnetite of selected samples from the Biwabik Iron Formation

Sample (core-depth [feet])	$\delta^{18}\text{O}_Q$ ‰ ± 1se	n	$\delta^{18}\text{O}_M$ ‰ ± 1se	n	$\Delta\text{QM}\%$
B2-2041.8	23.2 ± 1.1	4	-10.3 ± 1.1	6	33.6 ± 1.6
B2-2150.5	18.3 ± 0.7	8	-9.2 ± 0.7	3	27.6 ± 1.0
B5-1110	19.7 ± 0.4	10	-10.7 ± 1.0	8	30.5 ± 1.1
B5-1134	21.3 ± 1.2	3	-7.4 ± 0.4	8	28.7 ± 1.2
B5-745	23.7 ± 1.0	4	-4.9 ± 0.4	7	28.6 ± 1.1
B7-1146	24.2 ± 0.7	10	-6.4 ± 1.3	4	30.6 ± 1.5
B7-1206	22.0 ± 0.7	10	-3.6 ± 1.5	3	25.6 ± 1.7

mineral separates. This is a significant problem when performing bulk analysis on physically separated quartz and magnetite from these highly intergrown, fine-grained sediments. Contamination of the quartz by magnetite or vice versa would reduce the apparent fractionation and cause the values to plot further towards the metamorphic field. Secondly, ion probe analysis also ensures that there is no masking of isotopic heterogeneity inherent in the samples as a result of processes such as later stage veining and secondary mineral precipitation. For example, quartz is often present as a vein-filling mineral and, as such, is likely to have been crystallized at higher temperatures and from fluids of different isotopic composition than the microcrystalline quartz of the matrix of the main sedimentary banding which is assumed to be a recrystallization product of the original silica primary precipitate. Elimination of this isotopic homogenization of different generations and provenance of the two minerals also avoids a possible reduction in the apparent fractionation factor. The ion probe also allows isotopic ratios to be interpreted

within a framework of detailed petrographic analysis, which is not possible with conventional bulk measurements. There is textural evidence of disequilibrium, with the magnetite appearing to have crystallized later than the quartz, in a variety of mineralogical associations. This compliments the isotopic data which shows significant differences of up to 5.9‰ in the case of quartz and 7.2‰ in the case of magnetite between different samples which implies that the two minerals could have not formed from the same fluid at the same temperature throughout the formation. It can therefore be inferred that the quartz and magnetite have followed separate diagenetic pathways following burial of the primary precipitates and can not be used as a mineral pair geothermometer in unmetamorphosed Biwabik sediments. Generation of high resolution oxygen isotope data by the ion microprobe thus enables correlation with petrographic observations, eliminates problems of bulk sample contamination and isotopic homogenization and therefore greatly reduces interpretational uncertainty relative to conventional, bulk sampling methodologies.

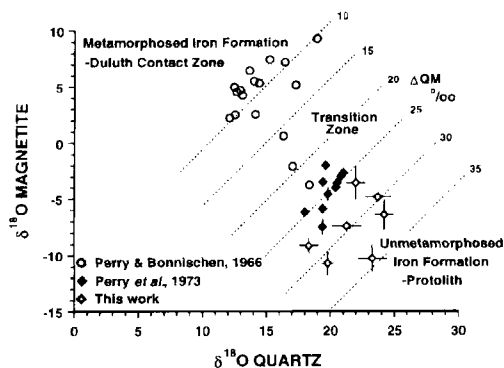


FIG. 1. $\delta^{18}\text{O}$ of quartz and magnetite from the Biwabik Iron Formation, Minnesota.

References

- Lyon, I.C., Saxton, J.M., Chatzitheodoridis, E. and Van Lierde, P. (1995) *Int. J. Mass Spec. Ion Proc.*, **144**, 1–16.
- Perry, E.C. and Bonnichsen, B. (1966) *Science*, **153**, 528–9.
- Perry, E.C., Tan, F.C. and Morey, G.B. (1973) *Econ. Geol.*, **68**, 1110–25.
- Pfleider, E.P., Morey, G.B. and Bleifuss, R.L. (1968) Mesabi Deep Drilling Project – Progress report (No.1) of Minn. Geol. Survey.
- Saxton, J.M., Lyon, I.C., Chatzitheodoridis, E., Perera, I.K., Van Lierde, P., Freedman, P. and Turner, G. (1996) *Int. J. Mass Spec. Ion Proc.*, **154**, 98–128.