Holocene climate record preserved in a ferricrete chronosequence from northern Yellowstone region

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Recent studies have shown that the oxygen isotope systematics of goethite (α -FeOOH) can preserve palaeoclimate information (e.g. Yapp, 1993). Here, we establish oxygen isotope ratios from goethite in ferricrete chronosequences as new source of Holocene climate information, and present a 9000 year proxy climate record from the Northern Yellowstone Region.

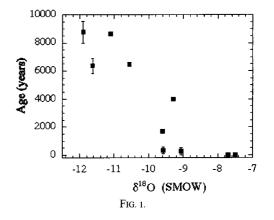
The ferricrete deposits are located approximately five kilometers from the northeast corner of Yellowstone National Park within the Fisher Creek (<10 km²) and Daisy Creek (<5 km²) drainages of the New World Mining District near Cooke City, Montana. Ferricrete formation is common in acidic drainages and here appears to have commenced shortly after glacial recession and exposure of iron sulphide-bearing ore bodies in the headwaters of both creeks. Ferricretes are presently exposed as 0.5-2 m. thick lenses of iron-oxide cemented terrace-deposits perched up to 2 m above the modern stream level. In addition, younger ferricretes are seen actively forming in the modern stream beds. Goethite is also seen precipitating out of modern streamwaters coating cobbles and tree branches in both Fisher and Daisy Creeks.

Ferricrete samples NW-1 through NW-7 (Table 1) were selected from age-stratified deposits located along the stream banks. The ages of these samples are constrained by ¹⁴C-dating of wood fragments either bracketing the sample or coated by a goethite crust (Table 1). These ages thus represent maximum ages of goethite precipitation, however it is unlikely that the actual ages of samples are significantly younger as iron-oxide precipitation and cementation appears to be relatively rapid. Sample 3-mod was taken from iron-oxide cemented gravels forming in the current Daisy Creek streambed. Though its absolute age is uncertain, we tentatively assign it an age of less than 500 years. Two samples, 2-mod and 6-mod, were scraped off of stream cobbles on which

goethite is actively being precipitated. These samples are considered modern and assigned an age of zero.

Samples were treated according to Yapp (1991), boiling them in 5M NaOH for 3 hours and washing them in 0.5M HCl for thirty minutes at room temperature. X-ray diffraction patterns show all samples to be well-crystallized goethite with no other crystalline iron-oxides present. Diffraction patterns were unaffected by NaOH and HCl treatments in all samples except NW-7, which showed significant improvement.

ICP whole-rock analyses show that all samples are variably contaminated with the weight percent impurities ranging from 0.8 to 18.3% (Table 1). It is assumed that impurities remaining after treatment are primarily detrital silicate minerals derived from the locally exposed igneous rocks. This assumption is justified by strong positive correlations (\mathbb{R}^{2} >.85) between the most abundant contaminating elements, suggesting variable contamination by detritus of uniform composition. The dominant lithology in the headwaters of both creeks is Tertiary felsic igneous rocks, which show chemical similarities to the sample contaminant. The fact that the major



Sample	Age (years)	Wt.% detritus	δ ¹⁸ O mixture	$\delta^{18}O$ goethite	% Yield goethite
 NW-1	8840-8700	2.64	-11.2	-11.9	98
NW-2	8620 ± 60	18.30	-7.2	-11.1	99
NW-3	6920-5810	4.38	-10.2, -10.5	-11.6	98
NW-4	550-100	12.47	-7.1, -6.8	-9.6	89
NW-5	1670 ± 40	2.50	-9.0	-9.6	99
NW-6	6490 ± 60	17.43	-6.8, -7.0	-10.6	94
NW-7	4000 ± 60	0.80	-9.1,-9.1	-9.3	90
2-mod	modern	16.58	-4.7	-7.7	100
3-mod	<500?	6.64	-7.6	-9.1	101
6-mod	modern	11.01	-5.4	-7.5	99

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contaminant in the goethite samples appears to be locally derived detritus allows for a simple massbalance calculation to determine the $\delta^{18}O$ of pure goethite.

Oxygen was extracted from the samples by hightemperature reaction with BrF_5 , converted to CO_2 in the presence of a heated graphite rod, and analysed on either a Finnegan 252 or Delta-E gas-source mass spectrometer. Precision is estimated to be ~0.25‰ (1 σ). Oxygen yields were determined manometrically for each sample and corrected for contamination (Table 1).

Oxygen isotope data are tabulated in Table 1 and plotted in Fig. 1. The data show a 3-4 per mil decrease in δ^{18} O of goethite over the past 9000 years. This change in δ^{18} O is too large to result solely from temperature dependent changes in the goethite-water isotope fractionation. Thus we infer that the δ^{18} O of the goethites are primarily recording changes in the δ^{18} O of the waters from which they precipitated. Mechanisms other than temperature, including a changes in dominant precipitation source or changes in the seasonal distribution of precipitation, may account for this isotopic trend. The greater Yellowstone region presently exhibits complex climate patterns reflecting the interaction of regional climate systems with local topography. Whitlock and Bartlein (1993) suggest that the northern Yellowstone region experienced a shift toward dryer summers since the early Holocene reflecting a decrease in summer precipitation derived from the Gulf of Mexico. In this scenario, we would expect an isotopic shift toward lower δ^{18} O values, as moisture originating in the Gulf of Mexico is typically isotopically heavier than moisture derived from the west. Though we can not immediately reconcile our data with this interpretation, we recognize the possibility that our climate proxy record reflects only very local changes and may not be suitable for characterizing the entire northern Yellowstone region.

References

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