

## Geology

### Oxygen isotope composition of human tooth enamel from medieval Greenland: Linking climate and society: Comment and Reply

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#### Notes

## Caledonian sole thrust of central East Greenland: A crustal-scale Devonian extensional detachment?: Comment and Reply

### COMMENT

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Hartz and Andresen (1995) have made a valuable contribution to central East Greenland Caledonian geology in their identification of a major extensional detachment separating high-grade gneisses and migmatites from the Eleonore Bay Supergroup. Essentially similar conclusions were reported by Strachan (1994) in the Ardencaple Fjord region, and there is now regional evidence that a large part of the East Greenland Caledonides was affected by crustal extension. This discussion is not directed to the conclusions of Hartz and Andresen's in central East Greenland, but to their discussion of  $^{40}\text{Ar}/^{39}\text{Ar}$  mineral cooling ages reported previously by us from the Ardencaple Fjord-Dronning Louise Land region in North-East Greenland (Dallmeyer et al., 1994).

Hartz and Andresen state that the  $^{40}\text{Ar}/^{39}\text{Ar}$  ages were interpreted by us to date "contractional deformation." This is not correct. We clearly stated in both the introductory and concluding parts of our paper that the ~438–370 Ma range of  $^{40}\text{Ar}/^{39}\text{Ar}$  mineral ages record cooling following a distinct polyphase metamorphic evolution, dated by U-Pb zircon methods at ~445 Ma and ~405 Ma. The only  $^{40}\text{Ar}/^{39}\text{Ar}$  ages reported to date closely deformational episodes were the ~393–385 Ma (Early Devonian) muscovite ages obtained from greenschist facies mylonites within part of the Dronning Louise Land thrust belt. We were careful to point out that "a tectonic framework for the polymetamorphic history . . . is necessarily speculative because of uncertainties in the timing of deformation events in relation to metamorphic episodes" (Dallmeyer et al., 1994, p. 624).

Hartz and Andresen further state that "on the basis of the recognition of major extensional shear zones, structures not reported by Dallmeyer et al. (1994), the most straightforward interpretation would be to relate at least the Late Silurian to Early Devonian cooling ages to uplift and erosion controlled by late orogenic collapse and not to contractional deformation" (Hartz and Andresen, 1995, p. 640). Once again, Hartz and Andresen do not cite our work accurately. The extensional shear zones of the Ardencaple Fjord region are clearly referred to in our paper where we stated that "formation of early nappe folds was post-dated by . . . extensional displacements along the Kildedalen and Bessel Fjord shear zones" (Dallmeyer et al., 1994, p. 617). In reference to these shear zones we noted (p. 623) that "constraints on the timing of extension are provided by U-Pb zircon ages of  $409 \pm 4$ – $9$  Ma and c. 400 Ma for emplacement of pre- to synkinematic granitoids."

Hartz and Andresen's interpretation of the  $^{40}\text{Ar}/^{39}\text{Ar}$  ages as dating mainly regional uplift controlled by late orogenic collapse conflicts with the field evidence reported by Friderichsen et al. (1994), Soper and Higgins (1993), and Strachan (1994) from the

Ardencaple Fjord region. In this area extension was followed by thrusting and northwest-southeast- to north-south-trending upright folding of the Eleonore Bay Supergroup and underlying supra-crustal sequences. Analogous upright folds are developed within basement gneisses exposed northwest and north of the Ardencaple Fjord region. They have been interpreted to have formed both during and after west-directed thrusting in Dronning Louise Land and strike-slip displacements along the Storstrømmen shear zone (Strachan et al., 1992; Dallmeyer et al., 1994). Although we agree with the evidence for regional extension in the East Greenland Caledonian belt, it is clear that the  $^{40}\text{Ar}/^{39}\text{Ar}$  ages reported by us in North-East Greenland date cooling following an Early Devonian contraction which was superimposed upon rocks that had already experienced crustal thickening and regional extension. The effects of late contraction can be shown to diminish southward when the regional-scale cross sections of North-East Greenland (Strachan et al., 1992; Strachan, 1994) are compared with those of central East Greenland (Henriksen, 1985). The above discussion implies that Early Devonian contraction in North-East Greenland was synchronous with continued crustal extension in central East Greenland and associated development of a Devonian supradetachment basin described by Hartz and Andresen. The oldest post-Caledonian sedimentary rocks exposed in North-East Greenland are Late Carboniferous (Piasecki et al., 1994). These are consistent with our view that following Early Devonian contraction, this part of the East Greenland Caledonian belt remained an area of positive relief throughout the Devonian and Early Carboniferous.

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## REPLY

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In a comment to our paper (Hartz and Andresen, 1995), Dallmeyer and Strachan disagree with our interpretation of their  $^{40}\text{Ar}/^{39}\text{Ar}$  white mica and amphibole age spectra from the Ardencaple–Dronning Louise Land region (Dallmeyer et al., 1994). In their model, they interpret  $^{40}\text{Ar}/^{39}\text{Ar}$  mineral age spectra, ranging between ~438 and 370 Ma, as dating cooling following polyphase metamorphic evolution. Clearly expressed in their comment, but not convincingly documented in the original papers (Dallmeyer et al., 1994; Strachan, 1994), are two contractional orogenic events (~445 Ma and ~405 Ma), both followed by extension. We disagree with this model as argued below, but agree with their statement that “a tectonic framework for the polymetamorphic history outlined above is necessarily speculative because of uncertainties in the timing of deformation events in relation to metamorphic episodes” (Dallmeyer et al., 1994, p. 624). Accordingly citations of their interpretations had to be general.

Dallmeyer and Strachan claim to have been cited incorrectly in regard to the recognition of major extensional shear zones. Although Dallmeyer and Strachan refer to extensional movement on the Bessel Fjord and Kildedalen shear zones, they are marked as thrusts and low-angle shear zones on their maps (Dallmeyer et al., 1994). More significant, however, is the relationship between these extensional faults, and the extensional shear zones below the Eleonore Bay Supergroup, in regard to the postulated superimposed Early Devonian contractional deformation and metamorphism. Published maps and cross sections (Dallmeyer et al., 1994; Strachan, 1994) show that these shear zones truncate folds in both the lower and upper plates. Abrupt change in metamorphic grade across the shear zone at the base of the Eleonore Bay Supergroup also supports post-peak metamorphic extension, which is responsible for exhumation of deep crustal rocks (Hartz and Andresen, 1995).

Dallmeyer and Strachan argue that our reinterpretation of the  $^{40}\text{Ar}/^{39}\text{Ar}$  ages are in conflict with field evidence. We disagree with this and feel that their orogenic model, requiring dramatic difference in structural style along the orogen, is controlled by a set of complex isotopic data not easily linked to structural or metamorphic events. One example is the Knæksø granite, which has given a U-Pb zircon age of ~382 Ma (Hansen et al., 1994), whereas muscovite from the same pluton has given an  $^{40}\text{Ar}/^{39}\text{Ar}$  cooling age of 432 Ma (Dallmeyer et al., 1994). Several of the cited Early Silurian ages are based on saddle-shaped  $^{40}\text{Ar}/^{39}\text{Ar}$  spectra from amphibole and should thus be treated with caution. Altogether, this makes it hard to accept that “it is clear that the  $^{40}\text{Ar}/^{39}\text{Ar}$  ages reported by us in North-East Greenland date cooling following an Early Devonian contraction which was superimposed upon rocks that had already experienced crustal thickening and regional extension.”

We regard an Early Devonian contractional event as an unnecessary complication and prefer to explain the available Ar data by Late Silurian to Middle Devonian extension and uplift. These data can easily be explained by Late Silurian to Middle Devonian extension. One example that supports this interpretation is the  $^{40}\text{Ar}/^{39}\text{Ar}$  muscovite ages from the Ardencaple area (Dallmeyer et al., 1994, Fig. 6). Here muscovite from granites in the hanging wall of the Kildedalen Shear Zone ranges between ~420 and 410 Ma. Mus-

covite from similar rocks in the basement below the shear zone range from 385 to 380 Ma. Instead of relating these two different age groups to two separate orogenic events, we interpret them as typical cooling ages found in areas undergoing large-scale crustal extension. In such a setting, the upper plate gives older ages, whereas the younger ages represent the time at which the lower plate was exhumed and cooled to the retention temperature for Ar in muscovite. Another area where a crustal-scale extensional model may explain the isotopic data is in Dronning Louise Land, where  $^{40}\text{Ar}/^{39}\text{Ar}$  ages of muscovite within the mylonites of the Storstrømmen Shear Zone range from 382 to 370 Ma, which Dallmeyer et al. (1994) and Dallmeyer and Strachan (Comment) argue date the strike-slip displacement. To us these ages represent uplift of an older (early Caledonian or pre-Caledonian) shear zone, along one or more detachments to the south and east.

Finally, Dallmeyer and Strachan comment on the lack of Devonian sediments in North-East Greenland, a feature they relate to Devonian contraction. The total thickness of post-Caledonian/pre-Jurassic (Late Carboniferous) sandstone in North-East Greenland is 25 m (Piasecki et al., 1994). We suggest that the lack of exposed late Paleozoic sediments in North-East Greenland is a consequence of the current erosional level and says little about late Caledonian basin evolution. In central East Greenland, there is 13 km of Devonian and Carboniferous sediments, deposited within supradetachment collapse basins (Hartz and Andresen, 1995).

On the basis of our own field data from central East Greenland and interpretation of field and isotopic data from North-East Greenland, we consider the Caledonides of central East and North-East Greenland to have undergone Late Ordovician through Silurian contractional deformation and metamorphism followed by orogenic collapse and extension (Hartz and Andresen, 1995). New  $^{40}\text{Ar}/^{39}\text{Ar}$  data (~420 Ma) on synextensional lamprophyres suggest that extension in central East Greenland was initiated in the late Middle to Late Silurian (Andresen et al., 1995), probably overlapping with thrusting in the foreland (Dallmeyer et al., 1994). As already argued (Hartz and Andresen, 1995), we consider this extension phase to continue through the Early and Middle Devonian, as documented by the collapse basins. We see no need to call upon a local Early Devonian contractional event in the Ardencaple Fjord to explain the existing database. The ~405 Ma U-Pb zircon age cited as evidence for the Early Devonian orogenic event is more likely associated with the synextensional magmatism (Hansen et al., 1994). During this extensional event, exhumation of the vast basement areas north of Bessel Fjord with Caledonian eclogites (Gilotti, 1995) took place.

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## Late Permian global coal hiatus linked to $^{13}\text{C}$ -depleted $\text{CO}_2$ flux into the atmosphere during the final consolidation of Pangea: Comment and Reply

### COMMENT

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Faure et al. (1995) suggest that  $^{13}\text{C}$ -depleted global  $\text{CO}_2$  levels recorded from coal seams support the existence of a Permian/Triassic (P/Tr) global event and global warming in the Triassic. The analyses of Faure et al. suggest a shift toward more negative  $\delta^{13}\text{C}$  values over the P/Tr boundary rather than toward more positive  $\delta^{13}\text{C}$  values. An overall trend toward positive values ( $^{13}\text{C}$ -enriched global  $\text{CO}_2$  levels) would be expected (Smith and Epstein, 1971), because the Triassic is known to be a warmer period than the Permian (Frakes et al., 1992). In addition to this, environmental parameters that would occur during warmer periods, such as water availability, increased light, and increased temperatures, positively shift  $\delta^{13}\text{C}$  values (O'Leary, 1988; Tieszen, 1991; van der Merwe and Medina, 1991).

Faure et al.'s main argument behind the significance of the  $\delta^{13}\text{C}$  shift and  $^{13}\text{C}$ -depleted global  $\text{CO}_2$  levels between the Permian and the Triassic is that Permian coals do not exhibit  $\delta^{13}\text{C}$  values lower than  $-24\text{‰}$ . However, earlier research (Jeffery et al., 1955; Compston, 1960) analyzed Permian and Triassic coals from Australia (excluding plant fragment analyses) and documented a  $\delta^{13}\text{C}$  range of  $-20.8\text{‰}$  to  $-27.3\text{‰}$  and  $-19.7\text{‰}$  to  $-24.9\text{‰}$ , respectively. Faure et al.'s assumption that  $\delta^{13}\text{C}$  values did not decrease below  $-24\text{‰}$  in the Permian, or increase above  $-24\text{‰}$  in the Triassic, is therefore invalid in light of this data. Their results indicate a more direct link with local  $^{13}\text{C}$ -depleted  $\text{CO}_2$  fluxes in South Africa. Hence, Faure et al.'s assumption that this is indicative of a global trend is incorrect in light of this evidence (Jeffery et al., 1955).

In addition, the  $\delta^{13}\text{C}$  shift between the late Permian and early Triassic, as documented by Faure et al., indicates a shift of only  $1.5\text{‰}$ . This shift is insignificant for several reasons.

(1) The  $\delta^{13}\text{C}$  shifts recorded in the Carboniferous and the Permian prior to the P/Tr event are far greater by recording shifts of  $\sim 2.5\text{‰}$  over smaller periods of geological time (Compston, 1960; Faure et al., 1995).

(2) The P/Tr boundary reflects one of the most catastrophic events in Earth's history (Erwin, 1993, references therein). A  $\delta^{13}\text{C}$  shift of  $\sim 1.5\text{‰}$  is negligible when taking into context the impact of the P/Tr event on environmental systems. In addition, the comparative shift between the Permian and Triassic recorded by Faure et al. is over a 15 m.y. interval ( $\sim 10$  m.y. from the P/Tr boundary and their Triassic coal analyses).

(3) The variations Faure et al. find in their  $\delta^{13}\text{C}$  trend from the Permian to the Triassic are within the range expected for floral ecosystems adjusting to environmental parameters. For example,

factors that can cause major variations in  $\delta^{13}\text{C}$  values on a localized scale include water stress (Guy et al., 1980), altitude (Körner et al., 1988), temperature (Tieszen, 1991), light levels (van der Merwe and Medina, 1991), and atmospheric  $\text{CO}_2$  levels (Polley et al., 1993).

It has been shown by Wickman (1953), Jeffery et al. (1955), Compston (1960), and Faure et al. (1995) that  $\delta^{13}\text{C}$  shifts occur at greater magnitudes during the Carboniferous, Permian, and Triassic periods. In addition to this, Permian and Triassic  $\delta^{13}\text{C}$  coal signatures are not restricted to values  $< -24\text{‰}$  and  $> -24\text{‰}$ , respectively (Jeffery et al., 1955). Current understanding of physiology, carbon isotope fractionation, and the effect of environmental parameters on plants suggests that Faure et al.'s interpretation of a  $\delta^{13}\text{C}$  shift of  $\sim 1.5\text{‰}$  from coal seams over the P/Tr boundary is at best speculative in view of greater  $\delta^{13}\text{C}$  shifts during the Permian and the Triassic.

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## REPLY

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Interpretation of the fossil record suggests that the largest mass extinction of life on Earth occurred during the Permian-Triassic (P-Tr) boundary period (see Erwin, 1993). This event coincides with several stable and radiogenic element anomalies recorded in the stratigraphic record throughout Pangea (Faure et al., 1995, Fig. 1 and references therein). One of the most remarkable anomalies is the global negative shift of  $\delta^{13}\text{C}$  values of marine carbonates across the P-Tr boundary. In addition, negative shifts in the  $\delta^{13}\text{C}$  values of marine organic matter (Magaritz et al., 1992) and terrestrial mammal fossils (Thackeray et al., 1990) have also been recorded. Several studies have speculated that one of the causes of the decrease in  $\delta^{13}\text{C}$  values of Earth's fluid envelope at that time are as a result of an organic carbon input and/or as a result of higher atmospheric  $p\text{CO}_2$  (e.g., Holser and Magaritz, 1987; Holser et al., 1989; Thackeray et al., 1990). In the Faure et al. (1995, Fig. 1) document we demonstrate that the "coal hiatus" in the global sedimentary record supports the hypothesis of a transfer of a large mass of terrestrial organic carbon (low  $\delta^{13}\text{C}$  value) into the biosphere. We also argue that the tectonic state of Pangea is consistent with the above hypotheses.

Criticisms of our paper by Gröcke include the following. (1) Because it has been postulated that globally climates became warmer in the Triassic, the  $\delta^{13}\text{C}$  values of coal have shifted in the wrong direction (i.e., the  $\delta^{13}\text{C}$  values should be more positive than in the Permian).

(2) Greater variations in  $\delta^{13}\text{C}$  values of coal occur in the Permian and Carboniferous prior to the P-Tr event.

(3) The overall shift ( $\sim 1.5\%$ ) to lower values in the Triassic coals is insignificant, especially considering changing environmental factors.

(4) In Australia, the values are not restricted to either  $> -24$  or  $< -24\%$  for the Permian and Triassic, respectively.

It has been demonstrated in several studies (see references in Faure et al., 1995, and Gröcke's Comment) that increasing temperature, water stress (drier), and irradiation, and decreasing "canopy effect" (less leaf cover) and osmotic stress all *increase* the  $\delta^{13}\text{C}$  value of C3 plants. The changes in the  $\delta^{13}\text{C}$  values are only relative and not quantitative. If one accepts the theory that climates did become hotter and drier in the Triassic (greenhouse state), then all the related environmental changes individually and collectively should produce a positive shift in  $\delta^{13}\text{C}$  values of the plant material. However, this is not the case as shown by the data reported in Faure et al. (1995). The clearly negative shift of  $1.5\%$  in Faure et al. (1995) is considered to be insignificant by Gröcke. We disagree and suggest that it must be significant and it would perhaps still be significant if the values did not change at all, considering that all the extreme environmental changes favor a positive shift. A positive shift of  $\delta^{13}\text{C}$  values of the vegetation must have been counteracted or offset by some other factor(s). We maintain that this was due to a massive  $^{13}\text{C}$ -depleted  $\text{CO}_2$  flux into the atmosphere, predominantly derived from oxidation of peat around the margins of the evolving Permian foreland basins of Pangea.

The negative shift in  $\delta^{13}\text{C}$  values of marine carbonates at the P-Tr is dramatic ( $6\%$ – $10\%$ ), occurs over a relatively short time span and, as is the case in the South African coals, have  $\delta^{13}\text{C}$  values

about  $1.5\%$  lower in the Triassic than the values before the P-Tr boundary (Holser et al., 1989; Magaritz et al., 1992). Greater variations in  $\delta^{13}\text{C}$  values of coal do occur in the Permian and Carboniferous prior to the P-Tr event, as pointed out by Gröcke, but the issue in the Faure et al. (1995) paper is the negative shift of  $\delta^{13}\text{C}$  values from the Permian to the Triassic. Globally no coal is preserved at the P-Tr boundary (the only time since the onset of formation of coal in the Devonian), so the  $\delta^{13}\text{C}$  anomaly is not recorded in the coal-bearing basins. A recent isotopic study in Australia of terrestrial organic matter preserved in Permian and Triassic age sediments reports that a negative shift of  $4\%$ – $8\%$  does occur across the P-Tr boundary (Morante et al., 1994).

The  $\delta^{13}\text{C}$  value of  $-24\%$  for the South African coal is not meant to be a quantitative value distinguishing global Permian and Triassic organic carbon, even though recent analyses (29 unpublished analyses) from other organic-bearing Early Permian sediments (Prince Albert, White Hill, and Collingham formations) in the Main Karoo Basin of South Africa also indicate that  $\delta^{13}\text{C}$  values are greater than  $-23.6\%$ , except for two values of  $-25.6\%$  and  $-24.1\%$ . It is not entirely surprising that the isotopic values from South African and Australian coals are different. In Australia, the coal deposits are widely distributed but are largely restricted to epicratonic portions of the Karoo Basin in South Africa (Hobday, 1987). The range and variation of microlithotypes, which will modify isotopic compositions, are controlled by the tectonic setting of the sediments.

We welcome Gröcke's questioning of our interpretations, but we feel that his criticism and supporting evidence is a little weak. The Faure et al. (1995) paper is based on a systematic isotopic study of specific coalfields, whereas the studies that Gröcke uses as reference for isotopic composition of Australian coals (Jeffery et al., 1955; Compston, 1960) are based on analyses of a few grab samples from several coal occurrences. We hope this discussion will help to sustain Gröcke's enthusiasm and will result in new chemostratigraphic research on the Australian coals so that some of his arguments do not have to be based on studies that were done more than 35 years ago.

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## Proterozoic low-Ti iron-oxide deposits in New York and New Jersey: Relation to Fe-oxide (Cu-U-Au-rare earth element) deposits and tectonic implications: Comment and Reply

### COMMENT

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Foose and McLelland's (1995) classification of the low-Ti magnetite bodies in the Adirondacks and Reading Prong-Hudson Highlands as Olympic Dam-type deposits is a welcome addition to the long-standing debate over these bodies. However, there are features of some deposits that suggest that the emplacement of the iron predated the main Grenville deformation and metamorphism and therefore cannot have been related to late tectonic granitoid emplacement as is implied by the assignment of the Olympic Dam model.

At many localities in both the Adirondacks and the Reading Prong-Hudson Highlands, the magnetite bodies have the form of isoclinal folds, suggesting that they experienced the same deformation that affected their enclosing rocks (see review in Skinner and Johnson, 1987). This basic observation was made in many of the early studies of the deposits, but in formulating genetic hypotheses it was generally de-emphasized in favor of what was perceived to be conflicting paragenetic and mineral textural information. Also, at Benson Mines, the largest and best known of the Adirondack deposits, the ores contain coarse sillimanite. The stability limits of sillimanite (Bohlen et al., 1991) require formation at deeper crustal levels and/or at higher temperatures than the 0–6 km depth and 150–600 °C ranges characteristic of Olympic Dam-type deposits (Hitzman et al., 1992). In fact, the silicate assemblages within the ores have been shown by Marcotty and Essene (1983) to have formed at 720 °C and 7 kbar (~19 km depth), pressure-temperature conditions indistinguishable from those of the regional Grenville metamorphism (Bohlen et al., 1985).

To support their proposed genetic connection between the magnetite bodies and late or posttectonic granitoid magmatism, Foose and McLelland cited late or posttectonic fracturing and fluid infiltration events that altered magnetite-bearing rocks. Although the magnetite bodies were affected by these events, it is important to note that there is no evidence that the same events were responsible for the initial emplacement of the iron. Similar alterations have been observed in both the Adirondacks and the Reading Prong-Hudson Highlands over wide areas and far removed from magnetite bodies (Johnson et al., 1990; Morrison and Valley, 1991; Cartwright et al., 1993). At localities removed from magnetite bodies, the alterations are associated with fractured and sheared rocks (Johnson et al., 1990; Cartwright et al., 1993). It has yet to be demonstrated that the typical association is alteration with magnetite bodies rather than alteration with fractured and sheared rocks irrespective of lithology. Further, the <sup>18</sup>O and K enrichments observed in the rocks are ambiguous evidence for a magmatic origin for the fluids because similar enrichments could be produced by virtually any fluid that had ascended through and reacted with the crystalline basement rocks at subsolidus or metamorphic temperatures.

With respect to the magnetite-bearing pegmatites associated with some magnetite bodies, there is no clear evidence that the parent melts were derived from late granitoid magmas. An alternative interpretation that is equally plausible is that the pegmatites were formed by partial melting of preexisting magnetite-rich rocks within the thermal aureoles of the intrusions. The contact meta-

morphic effects of the granitoid magmas have received little study, but there is clear evidence in the northwest Adirondacks that paragneisses on the flanks of a large syenite intrusion reached temperatures as high as 850–950 °C in an area where regional metamorphic temperatures were below 700 °C (Bohlen et al., 1985). Foose and McLelland asserted that the pegmatites formed "at depths much shallower than those of peak regional metamorphism" and are therefore compatible with the 0–6 km depths characteristic of Olympic Dam-type mineralization. I see no basis for such an assertion. In the absence of reliable geobarometric information, any estimate of the depth of formation of the pegmatites (or the veins or the hydrous skarn assemblages) must be considered speculative.

If low-Ti iron-rich deposits did predate the Grenville metamorphism, then there is reason to believe that they are genetically linked to other metamorphosed massive deposits such as the sphalerite-pyrite-(galena) deposits of the Balmat-Edwards district in New York, the pyrite deposits between Canton and Antwerp in New York, and the franklinite-willemitite-zincite deposits at Franklin Furnace and Sterling Hill in New Jersey. I have made the case elsewhere that these deposits are the products of hydrothermal systems that operated prior to the Grenville orogeny at shallow levels beneath the Proterozoic sea floor (Johnson et al., 1988; Johnson, 1990). The predominance of iron or zinc can be understood to reflect the distance of depositional sites from the sea-floor vent site or the topography of the ocean bottom. The presence or absence of sulfur can be understood to reflect the redox conditions at depositional sites. Analogues for the Adirondack and Reading Prong-Hudson Highlands deposits may be the massive sulfide and associated massive magnetite bodies in the Grenville Central Metasedimentary Belt of Quebec (Gauthier and Brown, 1986) and the zinc- and iron-rich deposits that are forming today beneath metalliferous brines on the floor of the Red Sea (e.g., Pautot et al., 1984).

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## REPLY

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Johnson questions our conclusions that (1) the low-Ti iron-oxide deposits of New York and New Jersey are late to posttectonic and (2) they formed at depths less than those of peak metamorphism. He notes that many of these iron deposits exhibit features consistent with a predeformation, premetamorphic origin, the most striking of which is the widespread concordance between some ore horizons and folded country rock. We specifically acknowledged this concordance in our paper; however, this feature only *suggests* a predeformational origin, but does not prove it. More conclusive are the ores that transgress lithologic contacts and crosscut metamorphic foliations, clearly demonstrating that mineralization postdates formation of the country rock as well as some deformation and metamorphism. Our paper specifically discusses the significance of these discordant ores as well as the absence of tectonic fabrics in many ores and their associated skarns. These straightforward field observations are wholly inconsistent with the formation of the low-Ti iron deposits prior to the intense polyphase deformation and metamorphism that affected the metasedimentary country rocks.

This preceding conclusion is confirmed by recent geochronologic studies of Lyon Mountain Gneiss, which hosts many of the Adirondack ore bodies, shows mutually crosscutting relationships with them, and therefore defines their maximum age. High precision, single grain U/Pb zircon geochronology fixes the age of Lyon Mountain Gneiss at  $1047 \pm 2$  Ma (McLelland and McLelland, 1996). By comparison, the age of the Ottawan orogeny has been constrained to ca. 1090–1045 Ma by McLelland and McLelland (1995, 1996), with the lower age determined by a single grain U/Pb zircon age of  $1045 \pm 4$  from an undeformed fayalite granite. These dates demonstrate that both Lyon Mountain Gneiss and their enclosed Fe-oxide ores are late- to posttectonic, as stated in our article.

Johnson notes the presence of sillimanite at Benson Mines and argues that it indicates greater pressure and/or temperature than Hitzman et al. (1992) consider to be characteristic of these deposits. We are well aware of the presence of sillimanite at Benson Mines and several other ore bodies, as well as in quartz-sillimanite veins and nodules within, and coeval with, Lyon Mountain Gneiss (Cunningham and Willis, 1996). Metamorphic zircons (McLelland and Chiarenzelli, 1990) and garnet (Mezger et al., 1991) within the Adirondack highlands yield ages of ca. 1050 Ma and demonstrate that sillimanite-grade temperatures prevailed during the emplacement of Lyon Mountain Gneiss. In addition, our paper specifically commented on the quartz-micropertite granite veins that crosscut ore

at Lyon Mountain. Clearly, temperatures were sufficient to form sillimanite during the deposition of some ores.

Good examples of late sillimanite occur at the Edison deposit (New Jersey), where unoriented, and thus posttectonic, sillimanite occurs in close association with ore. At Benson Mines, sillimanite occurs in Lyon Mountain Gneiss, in ores, and in country rock metasediments. The latter experienced high-grade regional Ottawan metamorphism and, as Johnson notes, have high-grade metamorphic assemblages. However, the metasediments predate the less intensely deformed and crosscutting iron ores (Leonard and Buddington, 1964). The depths and temperatures discussed by Hitzman et al. (1992) represent general conditions for the formation of the New Jersey and New York deposits, but locally conditions within deposits may vary significantly.

Johnson states that a genetic relation between iron deposits and rock alteration has not been shown and suggests that the alteration is a regional feature associated with any fractured and sheared rock. Although possible, we view this as unlikely. Because hydrothermal systems can alter rocks even if they do not deposit ore, Johnson's observation that altered rocks occur without magnetite does not constrain the relationship between alteration and ore deposition. On the other hand, the consistent association of magnetite deposits with pervasive K and Na alteration is remarkable, especially since reported occurrences of this kind of alteration away from magnetite deposits is relatively rare. We argue, as have previous workers (see Postel, 1952), that this association implies a genetic relationship.

Johnson also suggests that ore-associated magnetite-bearing pegmatites may result from the partial melting of iron-bearing metasediments in the contact aureoles of the Lyon Mountain Gneiss granite. If true, magnetite-rich country rocks should occur randomly and without association with Lyon Mountain Gneiss. This is not the case. Leonard and Buddington (1964) clearly demonstrated the close spatial association of magnetite deposits with "younger" granite, the relatively weakly deformed or undeformed granites that are now assigned to Lyon Mountain Gneiss. Further, these pegmatites have compositions similar to Lyon Mountain Gneiss, whereas a greater diversity of compositions would be expected if pegmatites had formed from the compositionally diverse country rocks. Finally, an undeformed magnetite-bearing quartz-albite pegmatite near Port Leyden (New York) crosscuts Lyon Mountain Gneiss and yields a U/Pb zircon age of  $1031 \pm$  Ma, whereas the compositionally similar host Lyon Mountain Gneiss yields  $1032 \pm 8$  Ma (Orell and McLelland, 1996). The correspondence in age and composition provides compelling evidence that the pegmatites represent a late fractionate from the Lyon Mountain Gneiss.

Finally, because detailed geobarometric information is absent, Johnson sees "no basis" for our suggestion that these deposits formed at depths less than those of peak metamorphism. However, the absence of such quantitative work does not preclude some qualitative conclusions. We believe the following clearly suggest temperatures and pressures less than those at peak granulite facies metamorphism. First, the profusion of quartz veins locally associated with these deposits implies the presence of substantial quantities of water that were not generally present during granulite metamorphism in the Adirondacks (Valley et al., 1990). Second, the evidence for hydraulic fracturing in many pegmatites indicates that fluid pressure exceeded lithostatic load. Although such fracturing could occur at any depth, exceeding lithostatic pressure would be easier under shallow conditions. Third, many ore-associated hydrous phases (particularly biotite) would not be stable under peak metamorphic conditions; their absence of tectonic fabric also shows that they postdate deformation. Finally, the association of jasper and chalcedony with some ore deposits (Postel, 1952) and of pumpellyite and



zoisite in others (Leonard and Buddington, 1964) could not have developed at great depth.

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## Oxygen isotope composition of human tooth enamel from medieval Greenland: Linking climate and society: Comment and Reply

### COMMENT

J. Daniel Bryant

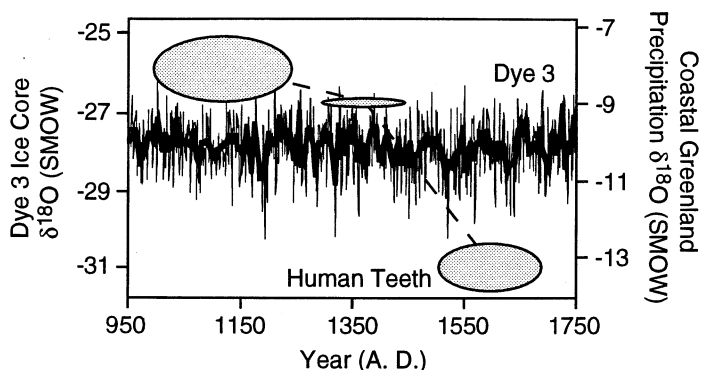
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Fricke et al. (1995) present a pilot study of the oxygen isotope composition of tooth enamel phosphate ( $\delta^{18}\text{O}_\text{P}$ ) of Norse and Inuit populations from coastal Greenland and Denmark to interpret the response of human societies to climate change. They document a 3‰ decrease in  $\delta^{18}\text{O}_\text{P}$  from the Medieval Optimum (~1000–1450 A.D.) to the Little Ice Age (~1500–1700 A.D.) at a series of sites near Julianehaab Bay in southern Greenland. If  $\delta^{18}\text{O}_\text{P}$  is recast as  $\delta^{18}\text{O}$  of precipitation using the linear relationship proposed by Longinelli (1984), this corresponds to a ~4.7‰ decrease in  $\delta^{18}\text{O}$  of precipitation. Fricke et al. (1995) interpret this shift as a Little Ice Age cooling event. Assuming  $\delta^{18}\text{O}_\text{P}$  of human teeth is linked only to  $\delta^{18}\text{O}$  of precipitation, we would expect to see a similar shift in the nearby Greenland ice cores. Yet the Dye 3 ice core (Dansgaard et al., 1982), located centrally to the Norse and Inuit sites analyzed by Fricke et al. (1995), shows no evidence of a dramatic shift in  $\delta^{18}\text{O}$  of precipitation during the Little Ice Age (Fig. 1). Although it may be possible to invoke climatic explanations for decoupling of the  $\delta^{18}\text{O}$  of precipitation from coastal to central Greenland, we here suggest alternative, biological mechanisms to explain the discrepancy between the human and ice-core oxygen isotope records.

One possible explanation is that  $\delta^{18}\text{O}_\text{P}$  varies as a function of tooth position. As noted by Fricke et al. (1995),  $\delta^{18}\text{O}_\text{P}$  of mammalian tooth enamel is an integrated record at constant temperature (~37 °C) of the  $\delta^{18}\text{O}$  of body water over the period of enamel mineralization. The  $\delta^{18}\text{O}$  of body water reflects the oxygen isotope mass balance of all throughputs (Luz et al., 1984; Bryant and Froelich, 1995) and is thus influenced not only by local meteoric or drinking water, but also by the  $\delta^{18}\text{O}$  of preformed water and metabolic oxygen in food and atmospheric  $\text{O}_2$ . For example, weaning reflects a fundamental shift in the oxygen isotope mass balance of a

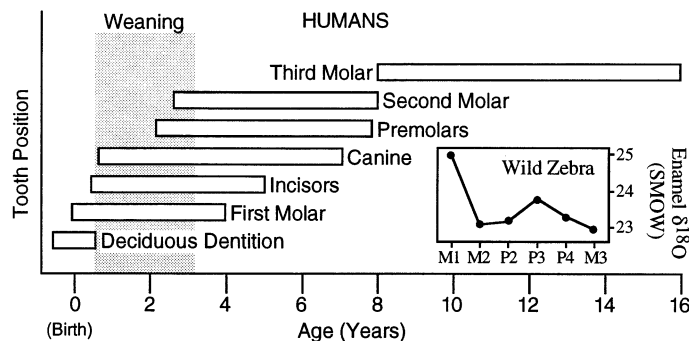


**Figure 1.** Comparison of  $\delta^{18}\text{O}$  of coastal Greenland precipitation reconstructed from human tooth enamel phosphate (Fricke et al., 1995) and  $\delta^{18}\text{O}$  from the Dye 3 ice core (Dansgaard et al., 1982). The vertical axis dimensions have different values but the same relative magnitude. The Dye 3  $\delta^{18}\text{O}$  record is presented with annual (thin line) and smoothed 5 yr average (thick line) resolutions. The Little Ice Age shift of 4.7‰ in  $\delta^{18}\text{O}$  of coastal precipitation at ~1500 A.D. implied by the oxygen isotopic composition of tooth enamel has no equivalent shift in the Dye 3  $\delta^{18}\text{O}$  record (<<2‰).

juvenile, because water in milk is in equilibrium with the body water of the mother from which it is derived and is enriched in  $^{18}\text{O}$  relative to drinking water (Wong et al., 1987). Thus the timing of enamel mineralization relative to weaning is critical (Fig. 2). In zebras the deciduous (juvenile) teeth and the first molar (the first permanent tooth to mineralize at or before weaning) may have  $\delta^{18}\text{O}_\text{P}$  values 2‰–3‰ different from teeth formed later (Fig. 2). Similar offsets might be expected in humans, in which weaning occurs between 6 mo to 3 yr of age (Ferry and Smith, 1983). This interval includes the timing of enamel mineralization of all the deciduous teeth and overlaps that of many of the permanent teeth (Fig. 2). Fricke et al. (1995) do not report the tooth positions analyzed, and thus it is unclear what impact this factor may have on the reported Little Ice Age shift in  $\delta^{18}\text{O}_\text{P}$ .

More interesting, the human samples analyzed by Fricke et al. (1995) from the Medieval Optimum at Julianehaab Bay are derived





**Figure 2.** Tooth enamel mineralization sequence and timing in humans (after Hillson, 1986), and an example of the effect of enamel mineralization sequence and timing on the  $\delta^{18}\text{O}$  of tooth enamel from a modern zebra (Bryant, 1995). In humans the age of mineralization of all but the third molar ("wisdom tooth") at least partly overlaps the observed range of weaning ages in humans; in zebras mineralization of the first molar (M1) completely or partly overlaps weaning. The sequence and timing shown are for upper teeth. The sequence is the same for lower teeth, but the timing may be slightly offset (by a few months to a year) relative to the upper teeth in humans.

from Norse colonies, whereas samples from the Little Ice Age with low  $\delta^{18}\text{O}_p$  are all derived from native Inuits. Culturally based differences in diet or food processing between the Norse and Inuits may contribute to differences in  $\delta^{18}\text{O}_p$ . For example, marine animals derive ingested water and food from seawater enriched in  $^{18}\text{O}$  and are  $^{18}\text{O}$ -enriched relative to terrestrial mammals that consume high-latitude surface waters and plants depleted in  $^{18}\text{O}$  (Nelson et al., 1986). Modeling studies suggest that the ratio of dietary fat, protein, and carbohydrate also influence the  $\delta^{18}\text{O}$  of body water and tooth enamel of animals (Tatner, 1988; Bryant and Froelich, 1995). Finally, while currently uninvestigated, differences in cooking and brewing of beverages has the potential to generate  $^{18}\text{O}$ -enriched foods due to preferential evaporative loss of  $^{16}\text{O}$ . Each of these biological signals may influence  $\delta^{18}\text{O}_p$ .

Our general point is that biological signals in animals with complex dietary and behavioral patterns, such as humans, may strongly influence the oxygen isotope composition of biogenic phosphate. None of the alternative explanations we propose can be constrained without additional data, and it is not clear if these biological influences are sufficiently large to explain entirely the discrepancy between the human and ice-core oxygen isotope records. Dietary influences and possibly even migration patterns may be constrained if  $\delta^{18}\text{O}_p$  analyses are coupled with examination of middens or with other isotopic tracers (e.g., Schoeninger et al., 1983; Nelson et al., 1986; Koch et al., 1995). Although  $\delta^{18}\text{O}_p$  of mammalian tooth enamel offers great promise for paleoclimatological, paleoecological, and paleobiological reconstruction, as with all tracers, the oxygen isotope systematics in complex biological systems must be quantified. More pilot studies such as that of Fricke et al. (1995) are needed to develop fully this novel tool.

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#### REPLY

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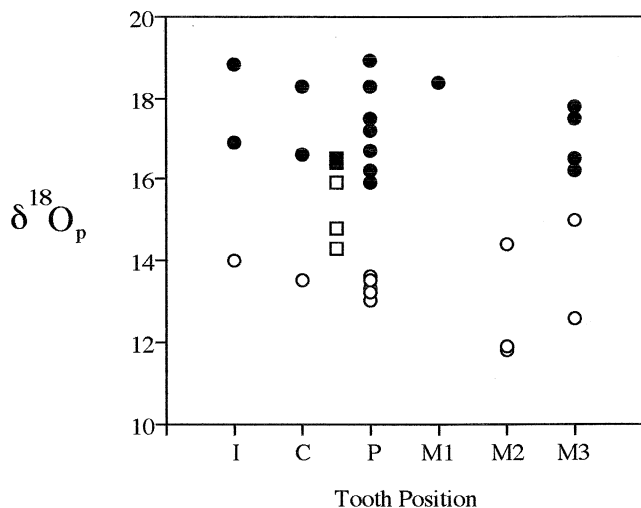
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We appreciate the interest of Bryant and Froelich in our pilot study of human tooth enamel phosphate (Fricke et al., 1995) and acknowledge that our observed shift in  $\delta^{18}\text{O}_p$  during the Little Ice Age in Greenland is more marked than any change in the mean annual  $\delta^{18}\text{O}$  values from the Dye 3 ice core ( $\delta^{18}\text{O}_i$ ). As a possible explanation, Bryant and Froelich describe how a Norse-Inuit sampling bias, or behavioral differences between these groups, could account for a large shift in  $\delta^{18}\text{O}_p$ . Data on tooth position and archaeological evidence, however, do not support this interpretation. It is more likely that geographic and hydrologic differences cause the enamel phosphate and ice-core records to respond to climate change in a different manner.

Bryant and Froelich state that tooth position is an important variable not included in Fricke et al. (1995). We provide here a plot of tooth position vs.  $\delta^{18}\text{O}_p$  (Fig. 1) to demonstrate that there is no systematic difference in  $\delta^{18}\text{O}_p$  between teeth, and that tooth position cannot account for the 3‰ difference between Norse and Inuit values. Because of the small tooth size, and slow rate of human dental development, the  $\delta^{18}\text{O}_p$  value for any one sample is an "average" value for enamel that formed over several years. Therefore any preweaning "signal," even in the first molars, incisors, and canines, does not appear to be dominant. In contrast, high crowned, rapidly forming teeth of large herbivores can record short-term changes in the isotopic composition of ingested water, and significant intertooth (e.g., the zebra of Bryant and Froelich's Comment) and even intratooth (bison and sheep of Fricke and O'Neil, 1996) variations in the  $\delta^{18}\text{O}_p$  values of enamel have been observed.

It is more difficult to account for isotopic effects arising from culturally based differences in diet and processing between the



**Figure 1.** Plot of tooth position vs.  $\delta^{18}\text{O}_p$  value. Filled and open symbols are Norse and Inuit samples, respectively. Squares rather than circles represent uncharacterized samples from either a canine or premolar.

Norse and Inuit. There is, however, zooarchaeological (McGovern, 1980) and carbon isotope evidence (Lynnerup, 1995) that suggests that the “average” Norse underwent a transition from a terrestrial to a marine-dominated diet over time, whereas the Inuit appear to have ingested a mix of terrestrial and marine resources. Because of this food source overlap, dietary differences between the Norse and Inuit cannot be responsible for their distinctly different  $\delta^{18}\text{O}_p$  values (although dietary differences may be the cause of the intrasite variations in  $\delta^{18}\text{O}_p$  values). As for resource processing, only the evaporation of water associated with cooking or boiling has the potential to affect  $\delta^{18}\text{O}$  radically. It is known from both historical and anthropological evidence that Greenland had a scarce supply of wood fuels, forcing them to rely instead on air-drying (e.g., Halfman et al., 1992). Brewing of beverages probably would have been limited as well. The Inuit who entered the region in later centuries would have had the same resource restrictions as the Norse and are thus unlikely to have had radically different food-processing strategies.

If the bulk of the 3‰ shift in  $\delta^{18}\text{O}_p$  is indeed a result of climate change, the central question to resolve is the lack of a comparable large isotopic shift in the Dye 3 ice-core data. The annual averages of  $\delta^{18}\text{O}_i$  presented by Bryant and Froelich could inadvertently obscure a signal of climate change. For example, there is a clear decrease of  $\sim 0.9\text{‰}$  in the seasonal averages of  $\delta^{18}\text{O}_i$  from the GISP2 ice core that Stuiver et al. (1995) attributed to cooling in the Little Ice Age. A more likely explanation is that the two isotopic records are so different that they would never react to climate change in the same manner, and therefore no one-to-one correspondence should

be expected. For example, the different geographic location of each site (coast vs. interior) will affect the amount, season, and form of precipitation, the relative humidity, wind speed, and wind direction. All of these variables influence the  $\delta^{18}\text{O}$  value of precipitation (e.g., Dansgaard, 1964) and could account for the different records of Little Ice Age cooling. More important, the two records are recording radically different things: The ice core sequentially preserves all secular variations in the  $\delta^{18}\text{O}$  of local precipitation, whereas  $\delta^{18}\text{O}_p$  is most strongly influenced by the  $\delta^{18}\text{O}$  value of stream or lake water ingested by humans. These surface water reservoirs are small, and their isotopic composition can be strongly influenced by ground water, which is biased toward winter precipitation (e.g., Maulé et al., 1994), by evaporation which occurs during snowmelt (e.g., Cooper et al., 1993), and by evaporation from the surface of the water bodies themselves. As such, ingested surface water may have a very different  $\delta^{18}\text{O}$  value than local precipitation.

Clearly more stable isotope research on geographic and hydrologic variations in this region needs to be conducted before quantitative comparisons between climate and different isotope records can be made. Until that time, simple comparisons of  $\delta^{18}\text{O}_p$  to  $\delta^{18}\text{O}_w$  (Fricke et al., 1995; Bryant and Froelich, above) must be made with care. The use of  $\delta^{18}\text{O}_p$  as a climate proxy is complicated, but the complementary behavioral and hydrological information that can be obtained from the analysis of materials from areas of human occupation make the effort worthwhile.

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