Regarding the validity of polar trace metal data: a response

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Summary. Boutron's comments are addressed. Evidence is presented suggesting that the high trace metal concentrations observed at a depth of 5.8–5.4 m at Dome C, east Antarctica and in a set of Arctic and Antarctic ice core samples I have analysed are real and not due to contamination. The importance of carrying out further trace metal studies in polar snow and ice is emphasized.

1 Regarding the AD 1909–13 concentration peak in Dome C snow

Dr Boutron has given several reasons why he feels his data for Dome C snows may be in error, thereby questioning the accuracy of the Tunguska mass estimate I have recently derived (LaViolette 1987a). It is indeed revealing that the two snow samples with highest heavy metal concentrations (5.8–5.4 m depth) were cored 5 to 45 cm below (directly under) the floor of a pit on whose surface equipment had been left to stand for a period of 3 yr. However, one cannot entirely dismiss the possibility that these heavy metal concentrations are, in fact, evidence of debris from the 1908 Tunguska explosion.

Several factors weigh in favour of this latter possibility. First, the peak is found in snows that date back to the time of this explosion event, AD 1912–16 ± 5 yr based on stable isotope dating, or AD 1909–13 ± 6 yr when these ages are recalibrated using the Krakatoa eruption as a time marker. Secondly, it is known that the Tunguska body was unusually rich in both Zn (19 per cent) and Pb (1.8 per cent) and that at this 5.8/5.4 m horizon these two elements register the most extreme increase of all the elements in Boutron's data set. For example, the Zn and Pb concentrations in that interval exceed the Zn and Pb means for his other 46 snow samples by 95 and 49 standard deviations. Also the Al/Fe and Zn/Fe ratios found at this horizon are very similar (within a factor of 4) to the ratios found in residues at the Tunguska explosion site. Thirdly, the concentrations are found to be highest in the lower 20 cm (5.8–5.6 m) of this 40-cm snow section, just as would be expected from a stratospheric fallout event. Fourthly, Ganapathy (1983) reports a fourfold increase in Ir in South Pole snows spanning the same period (AD ~1912–18 ± 4 yr recalibrated to AD 1908–14 yr) which he attributes to the Tunguska event. Moreover his Tunguska body mass estimate comes very close to the one I have derived from Boutron's data.

The relatively constant Na concentrations at this horizon observed by Boutron (1980) and

Legrand (1985) are consistent with the Tunguska-source hypothesis since the Tunguska debris would have raised the Na background level by only 3 per cent. In the case of K, a small increase would be expected, in fact, very close to the amount registered in Boutron's data. Levin & Bronshten (1986) have determined that the Tunguska body would have produced as little as 3×10^4 tons of nitric oxide upon entry through the atmosphere. If evenly distributed around the globe, this would have produced concentrations at Dome C averaging about $1 \mu g \, l^{-1}$ over a 2-yr period, well below the background level of $15 \mu g \, l^{-1}$ (Legrand & Delmas 1986). No comment can be made about the absence of increases in Cl, NH_4, and SO_4 across this time horizon since the abundances of these elements in Tunguska debris have not been established.

Boutron affirms that his Fe concentration values are reasonably accurate, except for systematic errors; so the Fe-based estimate for the mass of the Tunguska body should be all right. The Zn-based mass estimate should also be reasonably secure despite his suggestion that his Zn data may reflect contamination acquired during sample processing. For example, if the Zn concentration mean of his other 46 snow samples reflects the level of Zn contamination, then the magnitude of the Zn peak would be in error by only 1 per cent. Moreover, as Boutron (1980) points out, other peaks in his Zn data seem to be correctly placed relative to known volcanic eruptions (e.g. Krakatoa and Santamaria). So his Zn data does not seem all that implausible.

In view of the data corrections which Boutron (1988) gives for his Dome C results, the Fe and Zn excesses above background would increase to ~ 5.8 and $\sim 3.4 \mu g \, l^{-1}$, giving $\sim 48 \pm 30 \mu g \, l^{-1}$ for total dust contributed by the Tunguska event. Assuming a snow accumulation rate of $3.2 \, \mathrm{g \, cm^{-2} \, yr^{-1}}$ (after Thompson & Mosley-Thompson 1981), this gives a total dust mass for the Tunguska body of $(3.1 \pm 1.9) \times 10^6$ tons, not much different from my earlier estimate. As to the ultimate accuracy of this estimate, I agree that this matter cannot be definitively settled until more reliable ice core data become available for this time horizon.

2 Regarding the 12 dust samples filtered from prehistoric polar ice

Boutron questions the validity of geochemical measurements I have made on 12 samples of prehistoric polar ice (LaViolette 1983, 1985, 1987b). I agree with his suggestion that concentric veneers should be removed from each ice sample to establish a clear concentration plateau for the interior when conducting metals analysis. I had carried out my study in mid-1981 before there had been much discussion of the need for such precautions. Nevertheless, I believe that for the most part this data is sound. Until further measurements are made for these same trace metals in Camp Century and Byrd Station Wisconsin stage ice and until geochemical evidence of a contradictory nature is found, I see no reason for doubting the validity of these data.

Boutron suggests that the values I report for Ba, Sn, Sb, Ag and Ni reflect the entrainment of contamination clinging to the outer surface of the ice samples. He bases his hunch on past difficulties which he and others have had in measuring Pb in polar ice. However, measurement of Pb represents a worst case situation since concentrations of this element prevailing in today's environment are over 1000 times higher than abundances typical of the Earth's crust and of dust found in polar ice. Just the reverse is the case for Sn, Sb, Ag (which Boutron calls into question), as well as for Au and Ir, for which abundances in polar dust are found to range from 10^2 to 10^5 times crustal abundances.

The ice core decontamination procedure utilized by Thompson and myself was the same as that used by Herron *et al.* (1977) and Craigin *et al.* (1977). Ng & Patterson (1981) have shown that this procedure is effective in reducing surface Pb concentrations by 10^3–10^5-fold. Although they show that to obtain accurate values for Pb another order of magnitude reduction is required, realizable using their more recently developed veneer-chiselling procedure, it has not yet been determined

that such extreme precautions are absolutely necessary when measuring other trace elements in ice. For the majority of the elements that I measured, the situation should be similar to that for K, for which both decontamination procedures yield comparable results, e.g. compare Ng & Patterson (1981) with Craigin *et al.* (1977). In the case of precious metals such as Ir and Au, the risk of ice core surface contamination is even more unlikely (LaViolette 1985). In any case, to eliminate any doubt, future trace metal studies should analyse concentric ice core layers and establish inside–outside concentration profiles for each element.

The tin-rich Camp Century ice core dust sample (1234.7 m depth), discussed in previous *Monthly Notices* papers (Clube & Napier 1984; LaViolette 1987a), serves as an extreme example because of its high trace metal content. About 60 per cent of this sample consists of Sn, and high concentrations of Sb, Ag, Ir, Ni and Au are also found, with Ir, Ni, Fe and Co present in *chondritic proportions*. It does not seem possible that surface contamination could have introduced such high concentrations of one specific element, especially when ice core cleaning procedures were used that were capable of reducing surface contributions by up to 10^5-fold.

Regarding Thompson's (1977) laboratory procedures, although he processed his ice samples for microparticle counting and electron microprobe compositional analysis, rather than for whole sample trace metal analysis, this does not necessarily prove that Thompson's samples had become contaminated. His NaCl and sodium azide salt solution was filtered through a $0.45\,\mu$m filter before being added to his meltwater solutions. Also he frequently ran particle count blanks to ensure that his salt solutions were free of microparticle contaminants. To further ensure that this solution did not carry unwanted metals, I analysed a sample of NaCl from Thompson's laboratory and found it to be relatively free of Ir (LaViolette 1983, 1985). The spectra showed no signs of other heavy metals, such as Sn. Also, as a filter blank, I irradiated a clean edge of one of Thompson's dust-laden filter papers which, like the sample itself, was saturated with this 2 per cent salt solution. No excessive amounts of trace metals other than those inherent in the filter paper matrix were detected (LaViolette 1983, p. 543). In addition several blank Millipore filters were irradiated to determine the mean elemental contribution from the filter substrate so that this could be subtracted.

It is unlikely that the platinum electrode, which Thompson temporarily immersed in the meltwater solution during Coulter counting, could have contributed any substantial amounts of metals since platinum is very inert, even in a brine solution. Given the low electrode voltage, small surface area, and short immersion time, the number of Pt atoms that could have entered the solution would have been insignificant. No platinum peaks were seen in the spectra. Ganapathy's (1983) samples, which went through a similar treatment, could be used to establish upper limits to any suspected Ir contamination. The mean Ir concentration he found in his six samples, from which he calculated the steady-state cosmic dust deposition rate for that location, was 10–60 times lower than the concentrations I found in the Camp Century samples. Moreover Ir contamination seems unlikely even in the case of Ganapathy's samples since the cosmic dust deposition rate he derives appears to be in line with estimates made by other researchers.

To summarize, the points which Boutron brings up do indicate the need to carry out additional polar snow and ice core trace metal studies employing the precautionary measures which he suggests. I do not see, however, that this constitutes a serious challenge to my own ice core measurements and conclusions presented in past papers.

References

Boutron, C., 1980. *J. Geophys. Res.*, **85**, 7426.
Boutron, C., 1988. *Mon. Not. R. astr. Soc.*, **233**, 215.
Clube, S. V. M. & Napier, W. M., 1984. *Mon. Not. R. astr. Soc.*, **211**, 953.

Craigin, J. H. *et al.*, 1977. In: *Polar Oceans*, p. 617, Arctic Institute of North America.

Ganapathy, R., 1983. *Science,* **220,** 1158.

Herron, M. M. *et al.*, 1977. *Geochem. cosmochim. Acta,* **41,** 915.

LaViolette, P. A., 1983. *PhD dissertation*, Portland State University.

LaViolette, P. A., 1985. *Meteoritics,* **20,** 545.

LaViolette, P. A., 1987a. *Mon. Not. R. astr. Soc.,* **224,** 945.

LaViolette, P. A., 1987b. *Earth Moon Planets,* **37,** 241.

Legrand, M. R., 1985. *Doctorate thesis*, University de Grenoble, France.

Legrand, M. R. & Delmas, R. J., 1986. *Tellus,* **38B,** 236.

Levin, B. Yu. & Bronshten, V. A., 1986. *Meteorities,* **21,** 199.

Ng, A. & Patterson, C., 1981. *Geochim. cosmochim. Acta,* **45,** 2109.

Thompson, L. G., 1977. *Institute of Polar Studies, Rep. No. 64*, Ohio State University.

Thompson, L. G. & Mosley-Thompson, E., 1981. *Science,* **212,** 813.