Comment on “Next-Generation Ice Core Technology Reveals True Minimum Natural Levels of Lead (Pb) in the Atmosphere: Insights From the Black Death” by More et al.

**Todd Hinkley**

1 U.S. Geological Survey, Denver, CO, USA

**Plain Language Summary** More et al. (2017, https://doi.org/10.1002/2017GH000064) state that lead (Pb) concentrations in ice core from the high-altitude site Colle Gnifetti in Switzerland, reflecting atmospheric deposition over the past two millennia, have been consistently high because of human technological activity. They posit that abrupt departures toward smaller concentrations are caused by economic disruptions resulting from bubonic plague in the fourteenth and fifteenth centuries (plus a brief late nineteenth century economic depression), and by a decline in atmospheric injection of industrial Pb in the most recent few decades. Concentrations of Pb reported over those short anomalous intervals are very small, at least as small as in most pre-industrial Antarctic ice. More et al. believe that these intervals reflect natural, pre-anthropogenic levels. Their interpretation conflicts with a body of scientific information about the geochemical behavior and sources of Pb and how Pb is deposited by the atmosphere. To evaluate the validity of the interpretation of More et al. it is important to know (a) whether Pb in the ice is accompanied by other trace metals known to be present in natural sources; and (b) whether the isotopic composition of Pb in the ice is consistent with mined Pb or Pb from other, natural sources.

More et al. (2017, https://doi.org/10.1002/2017GH000064) state that lead (Pb) concentrations in ice core from the high-altitude site Colle Gnifetti in Switzerland, reflecting atmospheric deposition over the past two millennia, have been consistently high because of human technological activity. They posit that abrupt departures toward smaller concentrations are caused by economic disruptions resulting from bubonic plague in the fourteenth and fifteenth centuries (plus a brief late nineteenth century economic depression), and by a decline in atmospheric injection of industrial Pb in the most recent few decades. Concentrations of Pb reported over the short anomalous intervals that they associate with times of plague are very small, at least as small as in most pre-industrial Antarctic ice. More et al. believe that these intervals reflect natural, pre-anthropogenic levels. Their interpretation conflicts with a body of scientific information about the geochemical behavior and sources of Pb and how Pb is deposited by the atmosphere. To evaluate the validity of the interpretation of More et al. it is important to know (a) whether Pb in the ice is accompanied by other trace metals known to be present in natural sources; and (b) whether the isotopic composition of Pb in the ice is consistent with mined Pb or Pb from other, natural sources.

Their interpretation conflicts with a body of scientific information about the geochemical behavior and sources of Pb and how Pb is deposited by the atmosphere. To evaluate the validity of the interpretation of More et al. it is important to know (a) whether Pb, in both high-Pb and low-Pb ice samples, is or is not enriched relative to other metals known to accompany Pb from natural sources and whether those metals occur in the characteristic proportions of the known natural sources to the atmosphere and (b) whether the isotopic composition of Pb (208Pb/206Pb, 207Pb/206Pb, 204Pb/206Pb) in the ice is consistent with those of the mined European sources proposed by More et al. or whether there is isotopic evidence of Pb from other sources.

Considering the information about natural sources of Pb (viz., dust and volcano emissions) and the fact that those sources dominate the total amount of Pb in most preindustrial ice (Matsumoto & Hinkley, 2001), it is surprising that economic disruptions, however abrupt in time and magnitude, should cause abrupt and dramatic drops in Pb concentrations (Pb deposition) by 2 orders of magnitude for periods of only a few years in the fourteenth and fifteenth centuries. It is also surprising that there are no other drops in Pb concentration during the two millennia, either in the late years of the Roman Empire when legions probably could not continue their long-time work of capturing mine slaves from foreign territories or during Merovingian economic doldrums, perhaps finally ending with the opening of north German mines in the tenth century (e.g., Rommelsberg, 930 CE; Agricola, 1950, p. 5). It is necessary to develop some explanation or hypothesis.
about why Pb concentrations in ice should be so small in samples representing diminished economic activity (times of disease epidemic), lower even than many preindustrial Antarctic samples.

Quiescently degassing volcanoes worldwide preferentially emit Pb (approximately 1,000 tons per year) and a suite of other volatile metals to the atmosphere in distinct proportions, although there is some variability depending on volcanic rock type (Hinkley et al., 1994, 1999; Hinkley & Matsumoto, 2001). The metals Ag, Cd, Cu, In, Zn, As, Se, Sn, Sb, Te, Bi, and Au are, along with Pb, preferentially emitted by volcanoes, leaving behind the usually abundant elements of the Earth’s crust (Si, Ca, Mg, Na, K, Al, Fe, Ti, and Mg). If injection into the atmosphere of volcanic Pb were efficient, and if it were evenly distributed and eventually deposited by the atmosphere, a 10-cm-thick annual layer of ice would be expected to contain about 20-ng Pb/g of ice, or slightly less, from the volcanic emission source alone. (More et al. use units of nanogram per liter, which are nearly the same.) In fact, typical Holocene low-dust, preindustrial Antarctic ice may contain only about one third of this amount of Pb, indicating that some volcanic Pb may be lost during transport. Importantly, the proportions of metals are similar between volcano emissions and Antarctic ice. As mentioned, there is some variability in elemental proportions between volcanoes of different chemical rock types, and variability in metal ratios in ice core has been used to identify the types of volcanoes that have been dominant at particular times in the past (Hinkley & Matsumoto, 2007). In contrast, Pb emitted to the atmosphere from the mining and smelting of Pb ore is not accompanied by large and distinctive amounts of the suite of other metals.

More et al. acknowledge the possibility of a volcanic source as a component of Pb at Colle Gnifetti. They use a calculated parameter to evaluate the degree of volcanic association for the Pb in ice samples, called Pb crustal enrichment factors, or EFc. It is based on the amount of sulfur (S) present in the ice and the Pb/S in the ice. They acknowledge the limitation of the usefulness of the parameter, due to uncertainty about what fraction of total sulfur is volcanogenic. A more general limitation of the parameter is the complex and variable interaction of sulfur with the hydrologic cycle in the atmosphere. A more robust method to evaluate degree of volcanic origin for metals in ice may be to (a) measure the relative proportions of volcanically emitted metals, (b) determine the isotopic composition of Pb (see below), and (c) determine the rate of atmospheric deposition of metals into ice compared to rate of volcanic emission.

Lead present in dust derived from rock and soil may also be a major source of Pb to the atmosphere. When dust is very abundant in glacial ice (e.g., in Greenland and Antarctic ice strata deposited during dusty episodes corresponding to glacial “ice age” conditions), Pb from dust may dominate over volcanogenic Pb. In ice from dust-poor episodes corresponding to interglacial times (e.g., last 10 kyr), the relationship may be reversed. Most of the Colle Gnifetti samples are not dusty and not especially variable in their dust content. More et al. give information on the relation between amounts of Pb and amounts of dust, in the form of “enrichment factors,” which they base on their measurements of the dust proxy element titanium (Ti). If an enrichment factor is large, say, 30, it means that Pb in lattices of minerals in dust in the ice sample contributes only about one thirty-fifth of the total amount of Pb measured in the sample, the rest being accounted for by other “noncrustal” sources. More et al. do not discuss the meaning of variations in their data on Ca and Fe, which could represent proxy records for dust abundance in Colle Gnifetti ice, nor do they comment about the consistently high Ca/Fe ratios that suggests the dust present is dominantly carbonate.

The fine-grained fraction of atmospheric dust contains large amounts of certain trace elements, including Pb, compared to amounts in coarser rock dust particles assumed to have the “crustal values” (Engelbrecht & Derbyshire, 2010; Hinkley, 2014; Matsumoto & Hinkley, 2001). This extra trace element content in fine dust may be incorporated during atmospheric residence and transport, reflecting adsorption of volcanic components onto particle-reactive dust surfaces. Because of atmospheric mixing, it may have a globally homogeneous signature (Hinkley et al., 1997). At least in samples of preindustrial ice the relative proportions of volatile trace metals in the fine dust fractions are similar to proportions observed in volcanic emissions (Hinkley, 2014). Over longer periods of preindustrial time, soils may accumulate these atmospherically deposited metal-rich fine-grained materials and then remobilize them as their fine-grained fractions are again entrained into and transported by the atmosphere (Lal, 2007; Muhs et al., 2007), thus accounting for another atmospheric source of trace metals to glacial ice. This fine grained fraction in soils could be considered as a “buffer” to metals available to the atmosphere, both spatially and temporally, to both uptake and deposition of metals by the atmosphere: that is, because soils are geographically widespread, and always present as a...
Pb isotopes provide important information on the sources of Pb. The isotopes in Pb from the most numerous and strongly emitting quiescently degassing volcanoes are “radiogenic” (206Pb/207Pb values of 1.22 to 1.26, Hinkley, 2007, his Table 2; Sun, 1980). If the fraction of total Pb derived from dust in an ice sample of preindustrial age can be estimated (e.g., by means of some proxy for dust, such as Ca, Ba, Sc, Mn, or suites of lithogenic metals), then the contrasting isotopic composition of the rock dust and volcanic components can be calculated and distinguished. This was demonstrated for data by several workers on preindustrial ice from several Antarctic sites (EPICA Dome C, Taylor Dome, Coats Land, Law Dome, and Victoria Land; Hinkley, 2007, and references therein), showing that for any preindustrial Antarctic ice sample, the total amount of Pb can be modeled as a combination of volcanic Pb and dust Pb. In addition, it can be shown that the dust sources in those Antarctic samples and others may have somewhat different Pb isotopic compositions. That is, it is possible to “disentangle” and distinguish the isotopic compositions of the dust Pb and the volcanic Pb in suites of ice samples, if the amount of dust in the sample can be determined.

Isotopic compositions of mined Pb deposits vary, are well described from several major mining districts (Australia, Canada, United Kingdom, and Germany), and are generally substantially less radiogenic (i.e., low 206Pb/207Pb) than volcanic Pb. The isotopic composition of Pb from the Australian Broken Hill deposit, widely used throughout the world for many decades, is nonradiogenic and distinctive and has been identified as a component of some industrially contaminated young Antarctic ice samples (Vallelonga et al., 2005). Widely used Canadian ores are also nonradiogenic. British and German ores mentioned by More et al. as probable sources for the Pb in the Colle Gnifetti samples are nonradiogenic (typically 206Pb/207Pb of 1.17–1.19; e.g., Frere & Wilkes, 1989; Gardiner, 2001; Monna et al., 2000; Moorbath, 1962; Scaife et al., 2008). It should be possible to determine on the basis of isotopic ratios whether Pb from the dominant high-Pb samples at Colle Gnifetti is or is not dominantly from material processed from known mines or mining areas. If mined sources of Pb were important or dominant in some of the ice core from Colle Gniffeti, it might be possible to use the Pb/Ag ratio to identify input from particularly silver-poor British ores (Patterson, 1972, p. 226) compared to other European deposits.

Sea salt deposited from atmospheric aerosols is commonly abundant in glacial ice, and its proportion of the total load of impurities in ice can be determined (Matsumoto & Hinkley, 2001). Although the amount of Pb transported along with salt aerosols is minimal, salt content of ice is relevant to the broader geochemical and environmental picture. It is important to determine whether the amount of salt remained constant through two millennia at Colle Gnifetti, and whether it maintains a consistent relation to amount of mineral dust, and whether the abrupt declines recorded for Pb have any correlation with amount of salt.

Records of atmospheric deposition of trace elements into peat bogs in Europe and elsewhere do not show the same long-term high levels of deposition reported by More et al., through late antiquity, medieval, and early modern times, and the industrial revolution (Drexler et al., 2016, and refs. therein). Peat bogs preserve a less finely resolved time stratigraphic record than ice cores, but their records are robust over appropriate time spans.

In summary, the surprising analytical findings the interpretation presented by More et al. should not be uncritically accepted until additional investigations have been made. Perhaps some could be made by the More et al. group, some by other groups with different and additional analytical capabilities. These are the following:

1. An additional ice core (either existing in archives or newly bored) from Colle Gnifetti or comparable high Alpine site should be analyzed, at least in key time-stratigraphic intervals, to confirm that major features of the lead (Pb) concentration regime are the same as reported by More et al. (viz., consistent and high concentrations over about two millennia, except for very low concentrations in brief fourteenth and fifteenth century intervals; lowered concentrations in a nineteenth century economic depression, and in the most recent decades).
2. Additional analyses of the Colle Gnifetti and/or other appropriate core samples should be made to determine the following:

a. Whether lead (Pb) is or is not accompanied by a suite of other rare volatile metals that are known to accompany Pb in volcanic emissions and to be present in volcanic-dominated preindustrial Antarctic ice, in distinctive proportions. Absence (or different proportions) of such additional metals could indicate that the Pb in ice did indeed come from mines and smelting.

b. Whether the isotopic composition of the Pb in the Alpine ice (both in high-Pb and low-Pb intervals) has the radiogenic character of Pb in worldwide emission from quiescently degassing volcanoes or the nonradiogenic character of Pb in the European mine sources proposed by More et al. or other mines.

c. The amount of sea salt present in the Alpine ice should be determined, to better approach a full knowledge of the components of the total impurities in the ice. Also, more definitive characterization of the chemical composition of the rock dust present in the ice.

3. If the extremely low values reported for the brief fourteenth and fifteenth century intervals are verified, some explanation must be proposed for why they should be as low as they are, as low as or lower than most preindustrial, low-dust Antarctic ices.

It is not clear whether the analytical techniques employed by and available to the More et al. group could be used for the suggested additional investigations (above), especially those involving the measurement of proportions of isotopes of Pb (see Stoes-Gale & Gale, 2009) or whether it would be necessary to use more specialized but less rapid and less spatially resolved techniques, such as those involving thermal ionization mass spectrometry, with purification of Pb and other metals by means of ion exchange as part of the sample preparation procedure (Matsumoto & Hinkley, 1997).

Acknowledgments
This comment note benefited from constructive suggestions by C. Johnson, J. B. Paces, W. L. Ridley, and J. L. Slate, and from documentation research help from E. C. Wild.

References
Agricola, G. (1950). De Re Metallica, translation and notes (New York).

Drexler, J. Z., Alpers, C. N., Neymark, L. A., Paces, J. B., Taylor, H. E., & Fuller, C. C. (2016). A millennial-scale record of Pb and Hg contamination in peatlands of the Sacramento–San Joaquin Delta of California, USA. Science of the Total Environment, 551–552, 738–751. https://doi.org/10.1016/j.scitotenv.2016.01.201

Engelbrecht, J. P., & Derbyshire, E. (2010). Airborne mineral dust. Elements, 6(4), 241–246. https://doi.org/10.2113/gselements.6.4.241

Ferre, S. S., & Wilkes, J. J. (1989). Strageath: Excavations within the Roman fort 1973–85. London: Society for the Promotion of Roman Studies.

Gardiner, V. (2001). An analysis of Romano-British lead pigs. Institute forArchaeo-Metalurgical Studies Newsletter, 1, 11–13.

Hinkley, T. (2007). Lead in old Antarctic ice: Some from dust, some from other sources. Geophysical Research Letters, 34, L05B02. https://doi.org/10.1029/2006GL028736

Hinkley, T. K. (2014). Composition of airborne dust and time scales for buildup of trace elements in soils, DUST 2014, International Conference on Atmospheric Dust, Castellaneta Marina, Italy, June, 2014 (abstract).

Hinkley, T. K., Lamothe, P. J., Wilson, S. A., Finnegan, D. L., & Gerlach, T. M. (1999). Metal emissions from Kilauea, and a suggested revision of Moorbath, S. (1962). Lead isotope abundance studies on mineral occurrences in the British Isles and their geological significance. Philosophical Transactions of the Royal Society of London. Series A. Mathematical, Physical Sciences and Engineering, 354(1593), 175–181.

Hinkley, T. K., Le Cloarec, M.-F., & Lambert, G. (1994). Fractionation of families of major, minor, and trace metal suites. Geochemical Journal, 28(1), 1610–1610.

Lal, D. (2007). Recycling of cosmogenic nuclides after their removal from the atmosphere: Special case of appreciable transport of 10Be to polar regions by Aeolian dust. Earth and Planetary Science Letters, 264, 177–187.

Matsumoto, A., & Hinkley, T. K. (1997). Determination of lead, cadmium, indium, thallium and silver in ancient ices from Antarctica by isotope dilution-thermal ionization mass spectrometry. Geochemical Journal, 31(3), 175–181.

Matsumoto, A., & Hinkley, T. K. (2001). Trace metal suites in 75,000 years of Antarctic ice are consistent with emissions from quiescent degassing of volcanoes worldwide. Earth and Planetary Science Letters, 186, 33–43.

Mona, F., Hamer, K., Lévéque, J., & Sauer, M. (2000). Pb isotopes as a reliable marker of early mining and smelting in the Northern Harz province (Lower Saxony, Germany). Journal of Geochemical Exploration, 68(3), 201–210.

Moorbath, S. (1962). Lead isotope abundance studies on mineral occurrences in the British Isles and their geological significance. Philosophical Transactions of the Royal Society of London. Series A. Mathematical, Physical Sciences and Engineering, 354(1593), 175–181.

More, A. F., Spaulding, N. E., Bohleber, P., Handley, M. J., Hoffmann, H., Korotkikh, E. V., et al. (2017). Next-generation ice core technology reveals true minimum natural levels of lead (Pb) in the atmosphere: Insights from the Black Death. GeoHealth, 1, 211–219. https://doi.org/10.1002/2017GH000064

Muhs, D. R., Budahn, J., Reheis, M., Beann, J., Skipp, G., & Fisher, E. (2007). Airborne dust transport to the eastern Pacific Ocean off southern California: Evidence from San Clemente Island. Journal of Geophysical Research, 112, D13203. https://doi.org/10.1029/2006JD007577

Murozumi, M., Chow, T. J., & Patterson, C. (1969). Chemical concentrations of pollutant lead aerosols, terrestrial dusts and sea salts in Greenland and Antarctic snow strata. Geochimica et Cosmochimica Acta, 33(10), 1247–1294.

Hinkley, T. K., Matsumoto, A. (2001). Atmospheric regime of dust and salt through 75,000 years of Taylor Dome ice core: re...
Patterson, C. C. (1972). Silver stocks and losses in ancient and medieval times. *The Economic History Review, 25*(2), 205–235.

Scaife, B., Barreiro, B. A., McDonnell, J. G., & Pollard, A. M. (2008). Lead isotope ratios of 36 galenas from the Northern Pennines. Retrieved from http://www.brettscaife.net/lead/npennine/npennine.html

Stoes-Gale, Z. A., & Gale, N. H. (2009). Metal provenancing using isotopes and the Oxford archaeological lead isotope database (OXALID). *Archaeological and Anthropological Sciences, 1*(3), 195–213.

Sun, S. S. (1980). Lead isotopic study of young volcanic rocks from mid-ocean ridges, ocean islands, and island arcs. *Philosophical Transactions of the Royal Society of London. Series A. Mathematical, Physical Sciences and Engineering, 297*, 409–445.

Vallelonga, P., Gabrielli, P., Rosman, K. J. R., Barbante, C., & Boutron, C. (2005). A 220 kyr record of Pb isotopes at Dome C, Antarctica from analyses of the EPICA core. *Earth and Planetary Science Letters, 32*, L01706. https://doi.org/10.1029/2004GL021449