Pb-Pb isotope composition of the Flin Flon paleosols: Implications for oxidative weathering at ~1.85 Ga

Aisyah Abdkahar

Department of Geological Sciences, University of Manitoba, 125 Dysart Road, Winnipeg, Manitoba R3T 2N2, Canada; E-mail: aisyahk1@hotmail.com

Eirik Krogstad

Department of Geosciences, Georgia State University, 24 Peachtree Center Avenue SE, Suite 340, Atlanta, GA 30303, USA; E-mail: geoejk@langate.gsu.edu

Andrey Bekker

Department of Geological Sciences, University of Manitoba, 125 Dysart Road, Winnipeg, Manitoba R3T 2N2, Canada; E-mail: bekker@cc.umanitoba.ca

Summary

Pb-Pb isotope ratios were measured on 24 drillcore samples of the 1.85 Ga Flin Flon paleosol, adjacent siliciclastic and volcanoclastic sediments as well as volcanics, to determine the relationship between Th and U and its implications for oxidative weathering during the time of paleosol formation. Th/U ratios (κ_a) were calculated using the time-integrated equation (Pollack et al., 2009) that includes $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ initial ratios. The initial Pb isotope ratios that best satisfy the Flin Flon data were taken from the Superior Pb isotope model (Sinha and Tilton, 1973). Measured Pb isotope ratios indicate a closed system on a growth curve. Calculated κ_a values range from 1.97 to 3.36 and are lower than the upper crustal value of 3.8 (Taylor and McLennan, 1985) but are generally higher than κ_a values of the underlying volcanics and volcaniclastic sediments and matrix of the overlying conglomerates. The range of κ_a values in the paleosol as well as its relationship with that of the overlying and underlying immature sediments and volcanics suggest the decoupling of U and Th and, thus, oxidative weathering during the formation of the paleosol.

Introduction

Paleosols are the only direct proxies for atmospheric composition in the past (e.g., Rye and Holland, 1998; Pan and Stauffer, 2000). Paleosols older than 1.85 billion years are relatively uncommon and provide evidence for a different redox state and composition of the atmosphere and, potentially, much warmer climate at the time of their formation in contrast to more recent examples. Recent paleosols are much better preserved and much attention has been devoted to study their internal structures based on field and microscopic observations (Sheldon and Tabor, 2009). Whole rock geochemistry, such as trace element ratios (Sheldon, 2006), rare earth element concentrations (Nesbitt and Markovics, 1997), as well as stable isotope ratios, have been used extensively to reconstruct the provenance, atmospheric composition, and weathering processes based on the paleosol record. Radiogenic isotopes were rarely applied to the study of paleosols. In our study, the classical Flin Flon paleosol was examined by using field and petrographic observations as well as by analyzing Pb isotope ratios in an attempt to understand its implications for oxidative weathering at ~1.85 Ga. While U and Th are closely coupled and insoluble under reducing conditions, oxidative weathering decouples U and Th; therefore, Pb isotope composition provides a means to constrain the extent of this process.

Geological Setting

The Flin Flon paleosols occur at the contact between the Missi and Amisk groups (Holland et al., 1989; Pan and Stauffer, 2000) that belong to the Paleoproterozoic Flin Flon Domain of the Trans-Hudson Orogen (THO). The Amisk Group consists mainly of island-arc and ocean-floor mafic volcanic and sedimentary units that were deposited 1.92-1.84 Ga (Lucas et al., 1996). Unconformably overlying it is the molasse sediments of the Missi Formation; predominantly sandstones and conglomerates that were emplaced 1.84-1.854 Ga (Ansdell et al., 1992). The Flin Flon Domain is a complex collage of accreted terranes, sediments, and plutons that are part of the Paleoproterozoic arc assemblage of the Trans-Hudson Orogen of the Canadian Shield overprinted by greenschist facies metamorphism (Digel and Gordon, 1995).

Methodology

A total of 24 samples were prepared and analyzed at the Isotope Geochemistry Laboratory at the Georgia State University using whole rock Pb isotope methods that include digestion technique by Krogh (1973) and Pb column procedures. Th/U ratios, κ_a , were calculated using

the time-integrated equation
$$\kappa_a = \frac{\lambda_{238}}{\lambda_{232}} \times \frac{(^{208}Pb/^{204}Pb)_m - (^{208}Pb/^{204}Pb)_i}{(^{206}Pb/^{204}Pb)_m - (^{206}Pb/^{204}Pb)_i}$$
 (cf. Pollack et al., 2009)

where 'm' is the measured value and 'i' is the model initial value. The initial Pb isotope ratios that satisfy best to the Flin Flon data were taken from the Superior Pb isotope model (Sinha and Tilton, 1973).

Results and Discussion

Pb isotope ratios cluster on a 207 Pb/ 204 Pb vs. 206 Pb/ 204 Pb graph along a trend consistent with an age of ~1.9 Ga. This age is close to the depositional age of the paleosol which is ~1.85 Ga indicating that the paleosol and enclosing succession behaved as a closed system subsequent to deposition. κ_a values range from 1.97 to 3.36 and are lower than the upper crustal value of 3.8 (Taylor and McLennan, 1985) but are generally higher than κ_a values of the underlying volcanics and volcaniclastic sediments and matrix of the overlying conglomerates. The κ_a values fluctuate with depth and rock type (Fig. 1) indicating that U and Th were decoupled by oxidative weathering. The highest yielded κ_a value 3.36 is lower than the upper crustal value of 3.8 indicating that all samples were derived from a source enriched in uranium, which is consistent with κ_a values for the underlying volcanics and matrix from the overlying conglomerates. Geochemical data also suggests mixing of paleosol and unaltered volcanics on several levels within the paleosol suggesting local erosion and transport in a tectonically active environment. Figure 1 indicates a fluctuating trend of the uranium enrichment likely reflecting heterogeneity within the paleosol. This interpretation is also confirmed by petrographic observations of a variety of clasts in thin sections.

Conclusion

The 1.85 Ga Flin Flon paleosol has been characterized through the use of Pb isotope geochemistry. Modern soil structures are not present in the paleosol, except for the presence of basaltic corestones and onion-skin structures in a fine-grained matrix. The Flin Flon paleosol behaved as a closed system with respect to uranium and was formed by weathering of local volcanic sources in a tectonically active environment. It exhibits low ²³²Th/²³⁸U ratios that range from 1.97 to 3.36, which is lower than the upper crustal value of 3.8 (Taylor and McLennan 1985) thus suggesting decoupling of Th and U due to oxidative weathering. Heterogeneity is

observed throughout the paleosol unit both in clast abundances and in an enrichment and depletion in uranium.

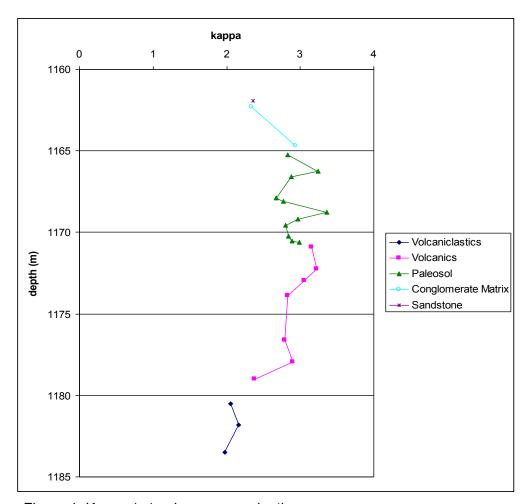


Figure 1. Kappa (ka) values versus depth.

Acknowledgements

Funding was provided by the Flin Flon Target Geoscience Initiative III project administered by the Geological Survey of Canada. Samples were provided by HudBay Minerals Inc. Thank you to David Price for field tours in the Flin Flon area, as well as Crawford Elliot for assistance in Georgia State University.

References

Ansdell, K.M., Kyser, T.K., Stauffer, M.R., Edwards, G. (1992): Age and source of detrital zircons from the Missi Formation: a Proterozoic molasse deposit, Trans-Hudson Orogen, Canada, *Canadian Journal of Earth Sciences*, Volume 29, pages 2583-2594.

- Digel, S., and Gordon, T.M. (1995): Phase relations in metabasites and pressure-temperature conditions at the prehnite-pumpellyite to greenshist facies transition, Flin Flon, Manitoba, Canada, *in* Schiffman, P., and Day, H.W., eds., Low-Grade metamorphism of mafic rocks: Geological Society of America Special Paper 296, pages 67-80.
- Holland, H.D., Feakes, C.R., and Zbinden, E.A. (1989): The Flin Flon paleosol and the composition of the atmosphere 1.8 bybp; *American Journal of Science*, Volume 289, pages 362-389.
- Krogh, T.E. (1973): A low-contamination method for hydrothermal decomposition of zircon and extraction of and Pb for isotopic age determinations, *Geochimica et Cosmochimia Acta*, Volume 37, pages 485-494.
- Lucas, S.B., Stern, R.A., Syme, E.C., Reilly, B.A., and Thomas, D.J. (1996): Intraoceanic tectonics and the development of continental crust: 1.92-1.84Ga evolution of the Flin Flon Belt, Canada, *Geological Society of America Bulletin*, Volume 108, No. 5, pages 602-629.
- Nesbitt, H.W., and Markovics, G. (1997): Weathering of granodioritic crust, long-term storage of elements in weathering profiles, and petrogenesis of siliciclastic sediments; *Geochimica et Cosmochimica Acta*, Volume 61, No.8, pages 1653-1670.
- Pan, Y., and Stauffer, M.R. (2000): Cerium anomaly and Th/U fractionation of the 1.85 Ga Flin Flon paleosol: Clues from REE- and U-rich accessory minerals and implications for paleoatmospheric reconstruction; *American Mineralogist*, Volume 85, pages 898-911.
- Pollack, G.D., Krogstad, E.J., Bekker, A. (2009): U-Th-Pb-REE systematics of organic rich shales from the ca. 2.15 Ga Sengoma Argillite Formation, Botswana: Evidence for oxidative continental weathering during the Great Oxidation Event; *Chemical Geology*, Volume 260, pages 172-185.
- Rye, R., and Holland, H. D. (1998): Paleosols and the evolution of atmospheric oxygen: a critical review, *American Journal of Science*, Volume 298, pages 621-672.
- Sinha, A.K. and G.R. Tilton. (1973): Isotopic evolution of common lead. *Geochimica et Cosmochimica Acta,* Volume 37, pages 1823-1849.
- Sheldon, N.D. (2006): Precambrian paleosols and atmospheric CO2 levels; *Precambrian Research*, Volume 147, pages 148-155.
- Sheldon, N.D., and Tabor, N.J. (2009): Quantitative paleoenvironmental and paleoclimatic reconstruction using paleosols; *Earth-Science Reviews*, Volume 95, pages 1-52.
- Taylor, S.R., and McLennan, S.M. (1985): The Continental Crust: Its composition and evolution. Blackwell, Oxford, 312 pages.