

# Weathering of granite under an O<sub>2</sub>- and CO<sub>2</sub>-rich atmosphere 2.45 Ga at Pronto, Ontario, Canada

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The palaeosols at Pronto, Ontario, Canada, developed at ~2.45 Ga on an Archaean granite. Although they have been studied by several investigators (e.g. Gay and Grandstaff, 1980; Mossman and Farrow, 1992), debates have continued as to whether or not a major loss of Fe occurred during the soil formation. Loss or retention of Fe during weathering is crucial in models for the evolution of atmospheric oxygen. The ambiguity of the data on the Pronto palaeosols was partly due to a possibility that some rock samples collected by previous investigators from the upper parts of the palaeosol section might represent foreign soils. Therefore, we have collected a suite of rock samples, including the parental granite, palaeosols, and overlying sedimentary rocks, at Pronto, and conducted a detailed mineralogical and geochemical investigation on these samples to elucidate the O<sub>2</sub> and CO<sub>2</sub> contents of the 2.45 Ga atmosphere. We have examined the changes in rock textures, mineral textures, mineral abundances, analysed the contents of major elements and 40 trace elements (including *REE*) of the bulk rock samples, and also analysed the major and *REE* contents of selected minerals using an electron microprobe analyser (EPMA).

## Petrology and mineralogy

The studied palaeosol section should be called as 'saprolite' or 'saprolith' rather than as 'palaeosol' in strict sense, because even the sample from the uppermost part of the section has retained some mineralogical and textural characteristics of the parental granite. The palaeosol section is unconformably overlain by a uraniferous conglomerate bed. The top part of the original palaeosol section, therefore, appears to have been eroded away during deposition of the overlying conglomerate beds. The true depth of the palaeosol section at Pronto is difficult to estimate because the exposures of the overlying

sediments are limited, the contact between palaeosol and overlying sediments is shallowly dipped, and because the surface exposures of palaeosols occur on a gently sloping hill. The total depth of the studied saprolith section is estimated to be around 20 m.

The parental rock is medium-grained pink granite. Its colour gradually changes through grey to yellowish grey, and its grain size to fine-grain toward the unconformity. The major minerals in the parental rock are plagioclase, quartz and microcline. Biotite and hornblende, which are partly altered to chlorite, are minor minerals. Apatite, allanite and sphene are observed as accessory minerals. The obscure texture of plagioclase, and the existence of chlorite and sphene suggest that the Archaean granite in this site underwent low grade metamorphism.

In palaeosols (saproliths), plagioclase is largely destroyed and is replaced by sericite. The relic of plagioclase remains in the lower part of the palaeosol. The size of original crystals, determined from the optical orientation of relic crystals, is almost the same as that in the parental granite. Orthoclase is much less destroyed but shows ragged-edges, and the relic texture is clear even at the upper most part of the saprolith near the unconformity. Sericite replaces the orthoclase. Quartz retains its original shape and size through the section. Hornblende, biotite and apatite begin to disappear in the lower part of the section. Fine grains of secondary monazite accompanied by iron- or *REE*-oxides, which are not observed in parent rock, are observed in sericite aggregates.

## Behaviour of ferric and ferrous irons

Concentrations of each oxide and element in the samples are normalized to TiO<sub>2</sub> or Ti in order to evaluate the true loss or gain during soil formation (cf. Ohmoto, 1996). Compared to the parental rock, the palaeosols have decreased the contents of Si, Ca,

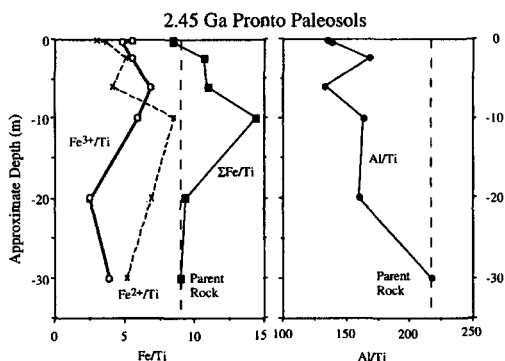


FIG. 1.

Na,  $\text{Fe}^{2+}$ , P, increased the contents of K,  $\text{Fe}^{3+}$ , but unchanged the contents of total Fe and Mg.

The retention of total iron, as indicated by nearly constant values of  $\sim 9$  for the  $\Sigma\text{Fe}/\text{Ti}$  ratios through the palaeosol section (except for one sample), and general trends of increasing  $\text{Fe}^{3+}/\text{Ti}$  ratios and decreasing  $\text{Fe}^{2+}/\text{Ti}$  ratios upward in the palaeosol section (see Fig. 1) are the most important characteristics of soils formed under an oxic atmosphere (Ohmoto, 1996).

Holland (1992) has suggested the following equation for the palaeosols which have retained Fe during weathering:

$$p\text{O}_2/p\text{CO}_2 = 0.4\text{Re} \quad (1)$$

where  $p\text{O}_2$  and  $p\text{CO}_2$  are, respectively, the partial pressure of  $\text{O}_2$  and  $\text{CO}_2$  of the atmosphere during soil formation, and Re is a measure of how much  $\text{O}_2$  and  $\text{CO}_2$  the parental rock can consume, and depends on the major element chemistry. Re value of the Pronto granite is 0.01. From a climatic model, Kasting (1993) has estimated the  $p\text{CO}_2$  value of  $\sim 10^{-1}$  atm (ca. 300 PAL) for the atmosphere around 2.5 Ga. Then, the palaeosol data at Pronto suggest that the  $p\text{O}_2$  value for the 2.45 Ga atmosphere was greater than about 0.0004 atm, i.e. greater than  $\sim 0.2\%$  of the present atmospheric level.

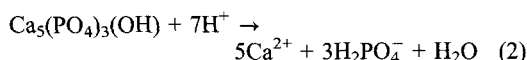
### Behaviour of aluminium

Al appears to have been lost during weathering as indicated by a decreasing trend of  $\text{Al}/\text{Ti}$  ratios upward in the palaeosol section (see Fig. 1). Major losses of Al are compatible with a model of higher  $p\text{CO}_2$  for the Precambrian atmosphere, because a higher  $p\text{CO}_2$  would have made the rainwater more acidic and because the solubility of  $\text{Al}(\text{OH})_3$  increases with increasing acidity. For example, with

a  $p\text{CO}_2$  value of 300 PAL, the pH of rain water becomes about 4.3 compared to the present value of 5.6, and the solubility of  $\text{Al}(\text{OH})_3$  increases from  $\sim 10^{-6}\text{M}$  to  $\sim 10^{-4}\text{M}$  (Stumm and Morgan, 1996).

### Behaviour of phosphorous and rare earth elements

Phosphorous in the parental rocks occur mostly in apatite, and the rare earth elements mostly in apatite, plagioclase, allanite and sphene. These minerals are essentially absent in the palaeosol section, probably because of reactions such as



The low-pH rain water would have favoured the dissolution of apatite and the other REE-bearing primary minerals. Destruction of most of these P- and REE-bearing primary minerals, however, did not cause most of the P and REE to be lost from the palaeosols; the P/Ti ratios of the palaeosols were reduced to only about 1/2 to 1/3 of the original values. Apparently, some of the P and most of the REE released from the dissolution of primary accessory minerals were reprecipitated as secondary monazite through reactions such as



In the palaeosol samples, small grains (up to 10  $\mu\text{m}$  in diameter) of monazite were observed, especially in the sericite-rich section.

### Conclusion

The 2.45 Ga palaeosol (saprolith) section at Pronto contain various geochemical characteristics of weathering of granite under an  $\text{O}_2$ - and  $\text{CO}_2$ -rich atmosphere.

### References

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