Appendices

I. Thermodynamic solubilities of Fe oxides, Al hydroxides, rutile, and silica at 25°C

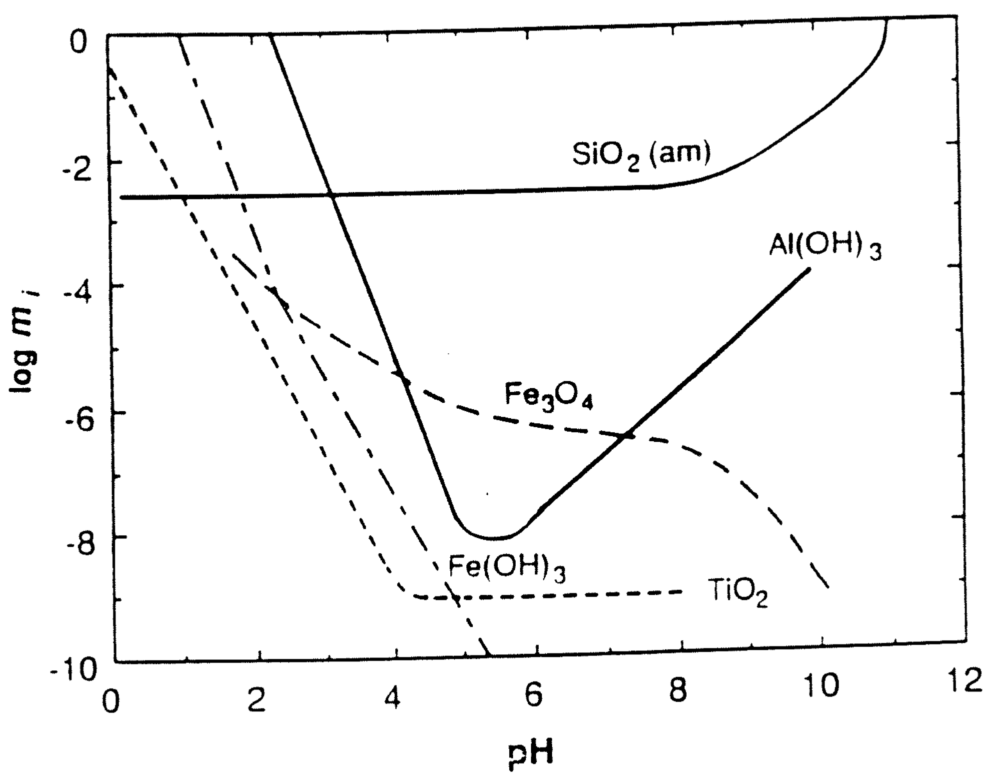
This diagram was constructed to show that the mobility of Ti is lower than Al in all pH conditions, and that the theoretical solubility of magnetite under a reduced condition is very high. The data source are:

SiO_2(am) and Fe(OH): Stumm and Morgan (1981)

$Al(OH)_3$: Wesolowski and Palmer (1994)

TiO_2 and $Ti(OH)_4$: Baes and Mesmer (1976) and Ziemniak et al. (1993).

Fe_3O_4: the solubility values are calculated for a condition of $P_{H2} = 10^{-3}$ atm from the experimental data of Tremaine and LeBlanc (1980) at T = 100°C and P_{H2} = 1 atm.



II. Kinetics of dissolution of magnetite

The following paragraph, presenting a detailed discussion on the sluggishness of magnetite dissolution reaction at low temperatures, is removed from the text because space limitation.

Theoretically, the solubility of magnetite in organic-free solution is controlled by the following reaction:

$$Fe_3O_4 \text{ (magnetite)} + H_2 + 6H^+ = 3Fe^{2+} + 4H_2O \qquad (1)$$

Solubility experiments on magnetite through reaction (1) have been carried out by several groups of investigators (Sweeton and Baes, 1970; Tremaine and LeBlanc, 1980) at temperatures up to 300 °C. The experiments were typically carried out using synthetic magnetite powders, rather than using natural crystals. Steady-state concentrations of Fe^{2+} in the experimental solutions were achieved in less than ~10 min even at temperatures as low as 50 °C. Such data give an impression that equilibrium is readily established in reaction 1 and that magnetite is easily dissolved in H_2-rich, low-temperature solutions. However, a close examination of the experimental data has revealed that the Fe^{2+} contents and the Fe^{3+}/Fe^{2+} ratios in solutions did not respond to the variations in the P_{H2} as expected from reaction 1, and the measured solubility values were several orders of magnitude less than the theoretical solubility values at all temperatures. Such findings suggest that the Fe^{2+} measured in the experimental solutions came from dissolution of "unstable" FeO on the surfaces and edges of synthetic magnetite, rather than from dissolution of both FeO and Fe_2O_3 in the magnetite crystal lattice.

Reductive dissolution of Fe_3O_4 and the attainment of the theoretical solubility values for magnetite in organic-free solutions appear to be very difficult at near-surface temperatures. For example, it took ~2000 h for Kishima and Sakai (1984) to reduce hematite (Fe_2O_3) to magnetite by H_2-rich aqueous solutions and to attain equilibrium among H_2, Fe^{2+} and Fe^{3+} species in aqueous solutions at 300 °C. This reaction rate is about two orders of magnitude slower than that to reduce aqueous sulfate (S^{6+} species) to H_2S (S^{2-} species) by H_2 and to attain equilibrium among H_2, S^{2-}, and S^{6+}-species at the same temperature (Ohmoto and Lasaga, 1982). At 25 °C, it takes more than

10^9 yr to achieve equilibrium among H_2, S^{2-}, and S^{6+} species. Although there is a lack of experimental data, it is probable that more than 1 b.y. are also required to attain equilibrium among H_2, Fe^{2+}, and Fe^{3+}-species even when the P_{H2} is as high as 10^{-3} atm and pH is as low as 4.5. In other words, significant dissolution of magnetite (and other Fe^{3+}-minerals) is unlikely to occur by an inorganic mechanism during the formation of a soil profile which typically completes in less than 10 m.y.

The above suggestion is supported by White et al. (1994) who have shown experimentally that the long-term dissolution rates of magnetite under an anoxic condition is much slower than those proposed by previous investigators, and that sand-size grains of magnetite will persist more than 10 m.y. during weathering.

III. Depth profiles of Fe^{3+}/Ti, Fe^{2+}/Ti, and $\sum$Fe/Ti ratios, and Fe^{3+}/Ti vs Fe^{2+}/Ti plots of paleosols examined in this study

They are arranged in order of decreasing age: Pre-Pongola (3.0-2.8 Ga), Dominion (2.9-2.8 Ga), Villebon (2.75 Ga), Mt. Roe (2.75 Ga), Hokkalampi (2.5-2.2 Ga), Ville Marie (2.45-2.2 Ga), Denison (2.45-2.25 Ga), Pronto (2.4-2.3 Ga), Quirke II - DDH270 (2.4 Ga), Hekpoort (2.2 Ga), Drakenstein (2.2-2.0 Ga), Flin Flon-1 (1.8 Ga), Flin Flon-2 (1.8 Ga), Athabaska-20 (1.5 Ga), Athabaska-81 (1.5 Ga), Drake (350 Ma), and Barynton (modern).

References for Appendices (excluding those included in the text)

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Macdonald, C. C., 1980, Mineralogy and geochemistry of a Precambrian regolith in the Athabaska Basin: Master's thesis, Saskatoon, Canada, University of Saskatchewan (quoted in Holland, 1984).

Macfarlane, A. W., Danielson, A., and Holland, H. D., 1994, Geology and major and trace element chemistry of late Archean weathering profiles in the Fortescue Group, Western Australia: Implications for atmospheric P_{O2}: Precambrian Research, v. 65, p. 297-317.

Nesbitt, H. W., and Wilson, R. E., 1992, Recent chemical weathering of basalts: American Journal of Science, v. 292, p. 740-771.

Ohmoto, H., and Lasaga, A. C., 1982, Kinetics of reactions between aqueous sulfates and sulfides in hydrothermal systems: Geochimica et Cosmochimica Acta, v. 46, p. 1727-1745.

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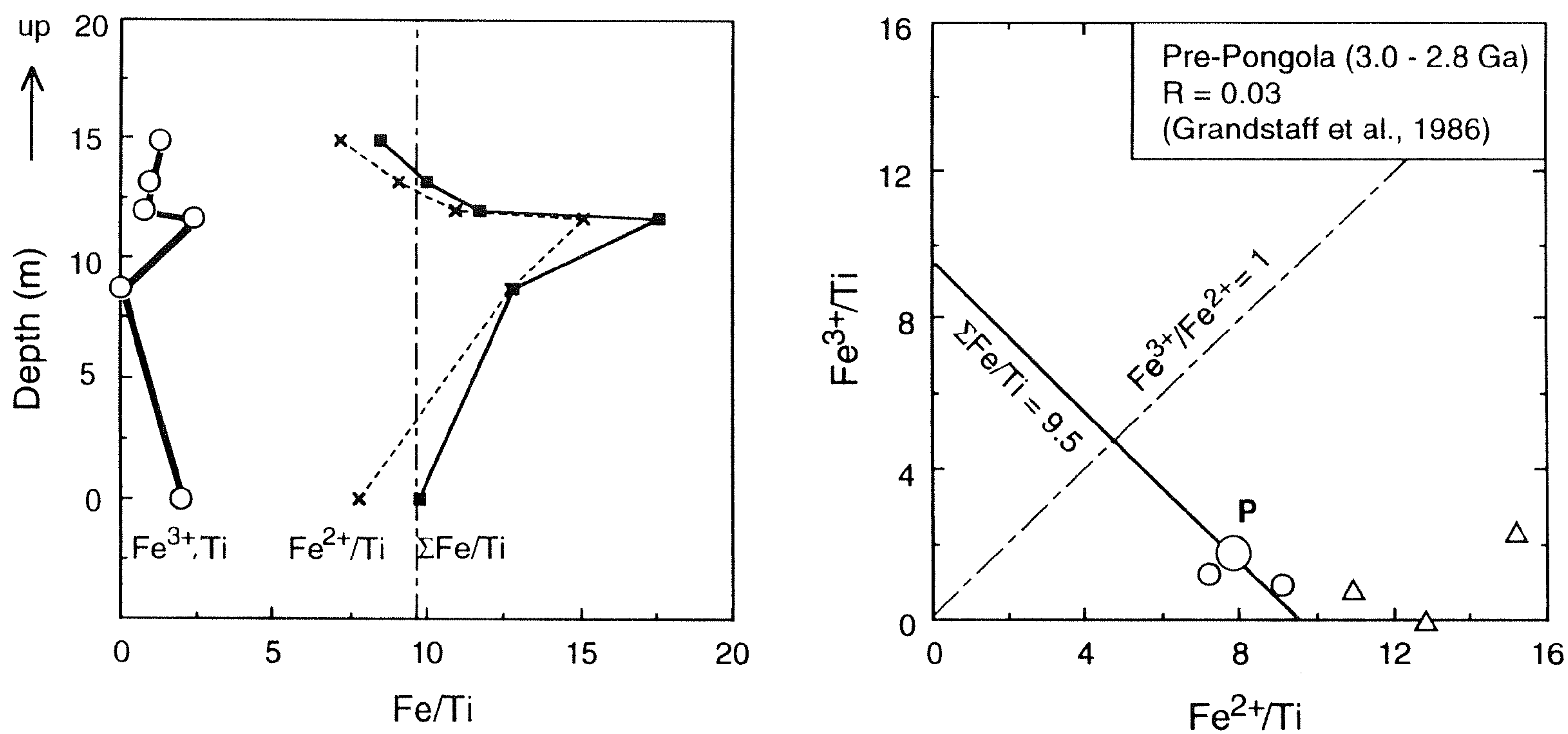
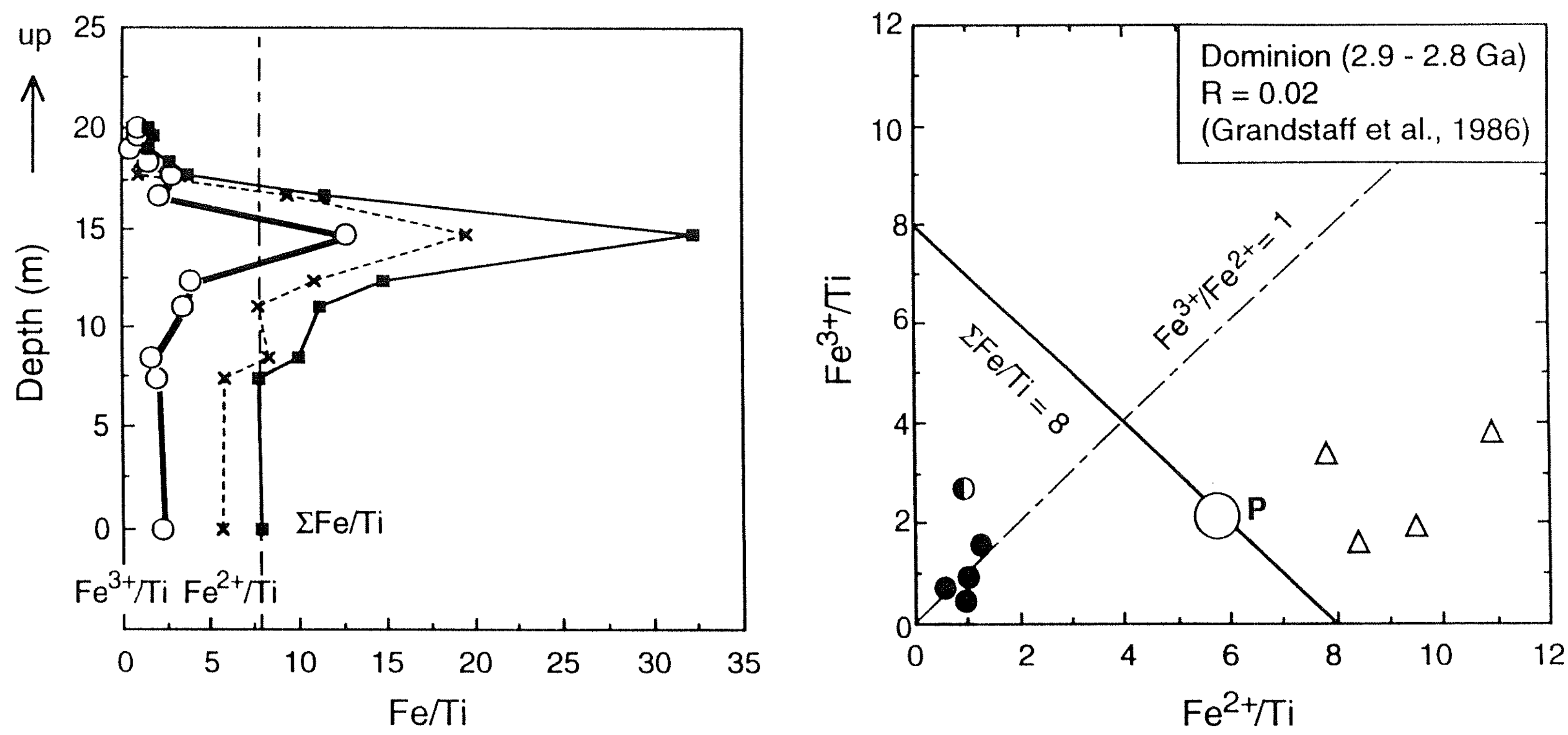
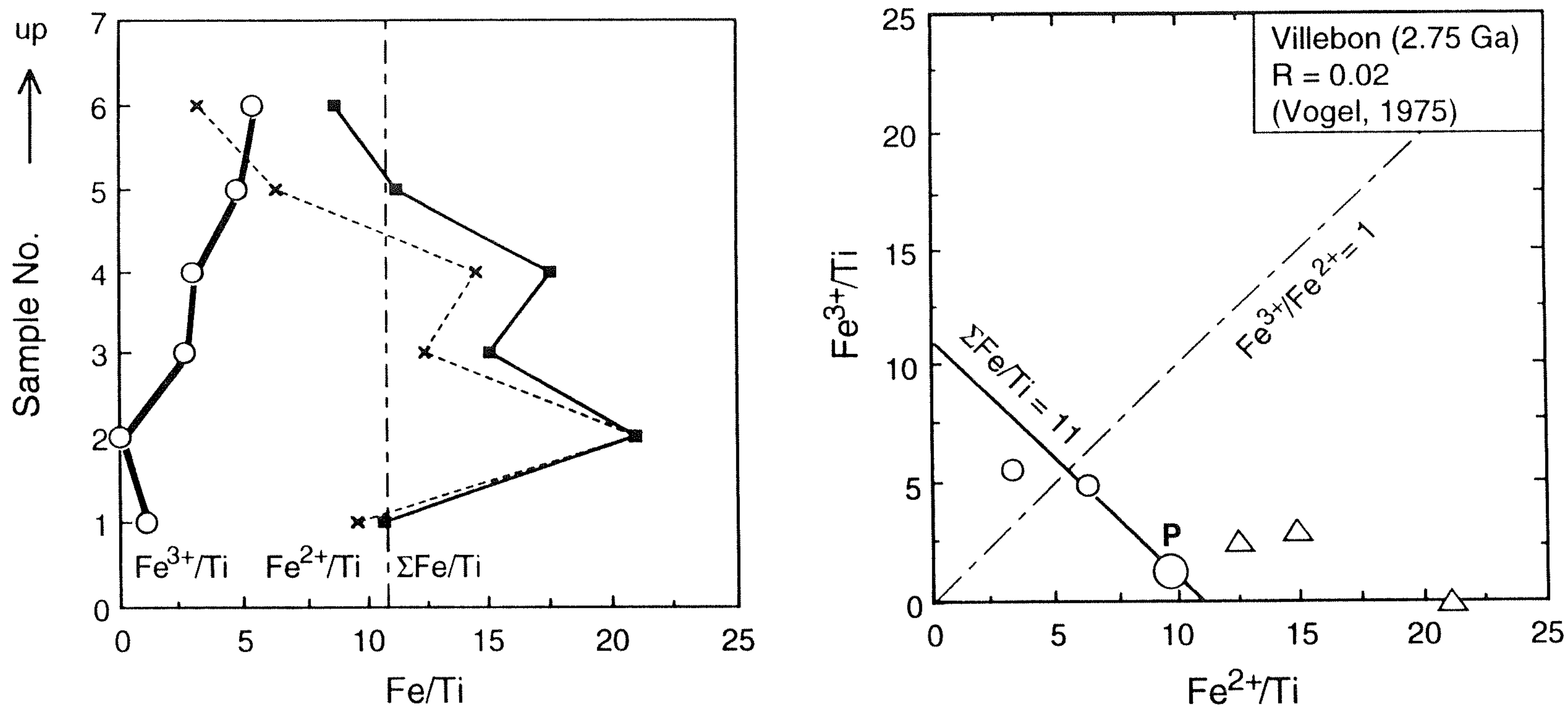
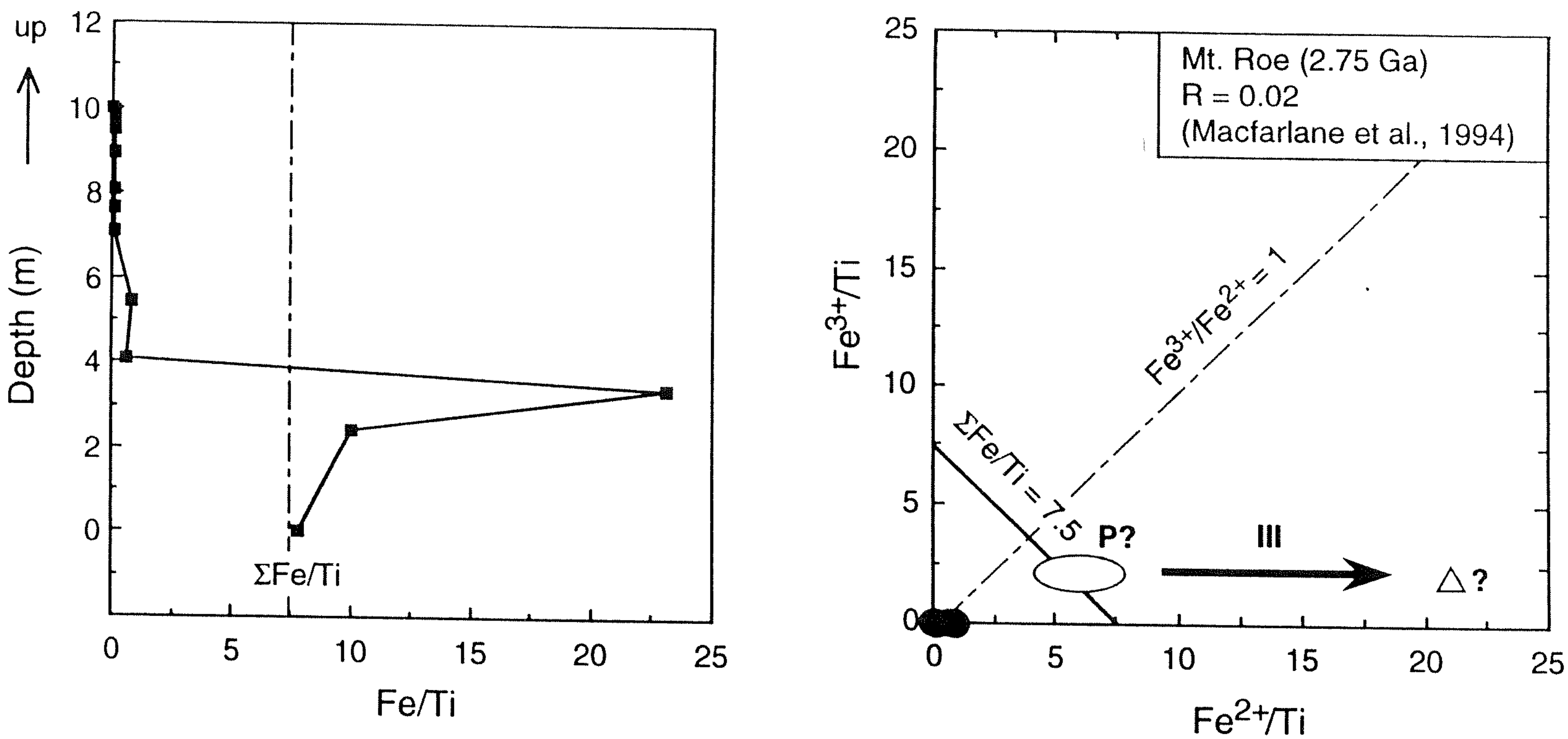


up
Depth (m)
Fe/Ti
Fe3+/Ti
Fe2+/Ti
ΣFe/Ti
Pre-Pongola (3.0 - 2.8 Ga)
R = 0.03
(Grandstaff et al., 1986)
ΣFe/Ti = 9.5
Fe3+/Fe2+ = 1
P

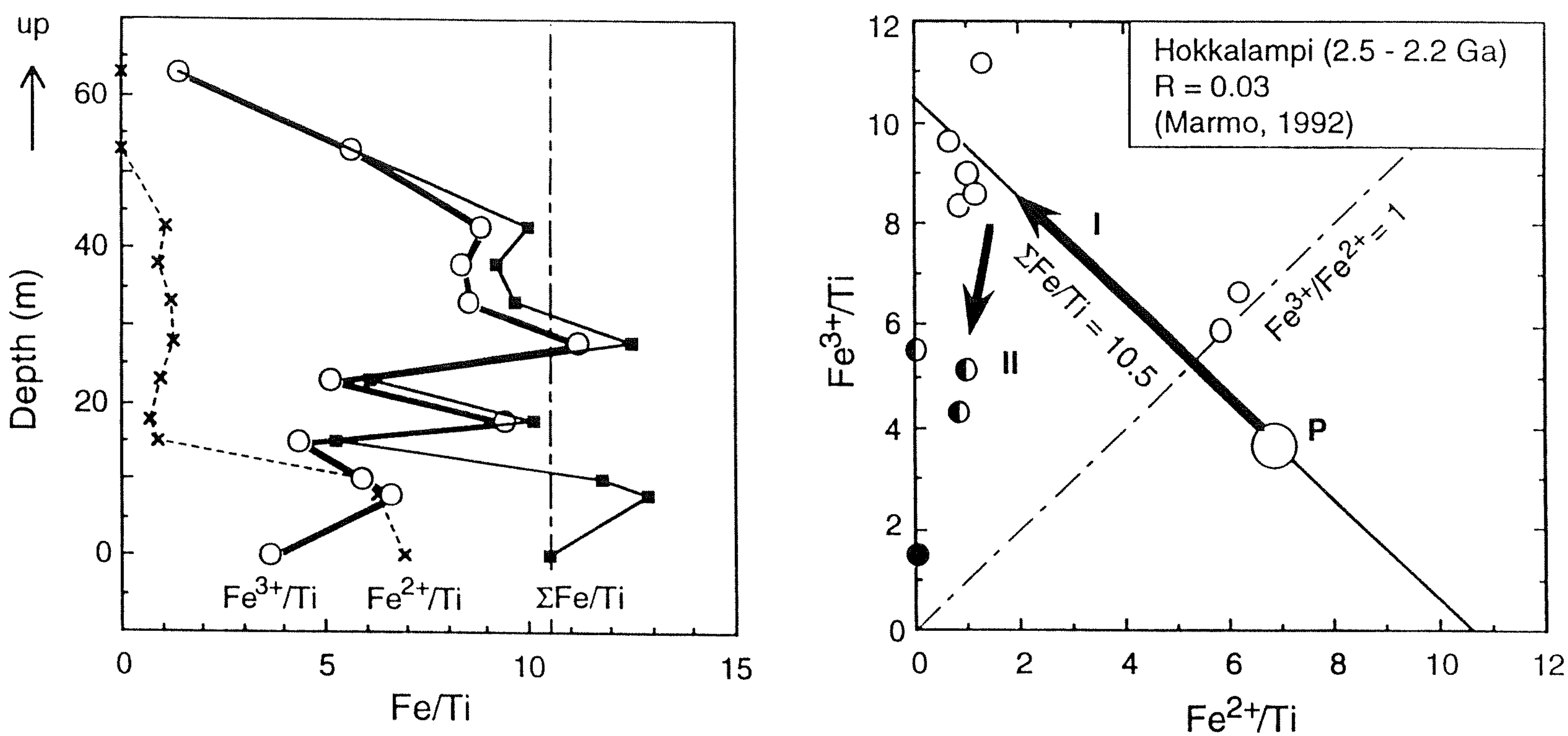


up
Depth (m)
Fe/Ti
Fe^{3+}/Ti
Fe^{2+}/Ti
ΣFe/Ti
Dominion (2.9 - 2.8 Ga)
R = 0.02
(Grandstaff et al., 1986)
ΣFe/Ti = 8
$Fe^{3+}/Fe^{2+} = 1$
P
Fe^{3+}/Ti
Fe^{2+}/Ti

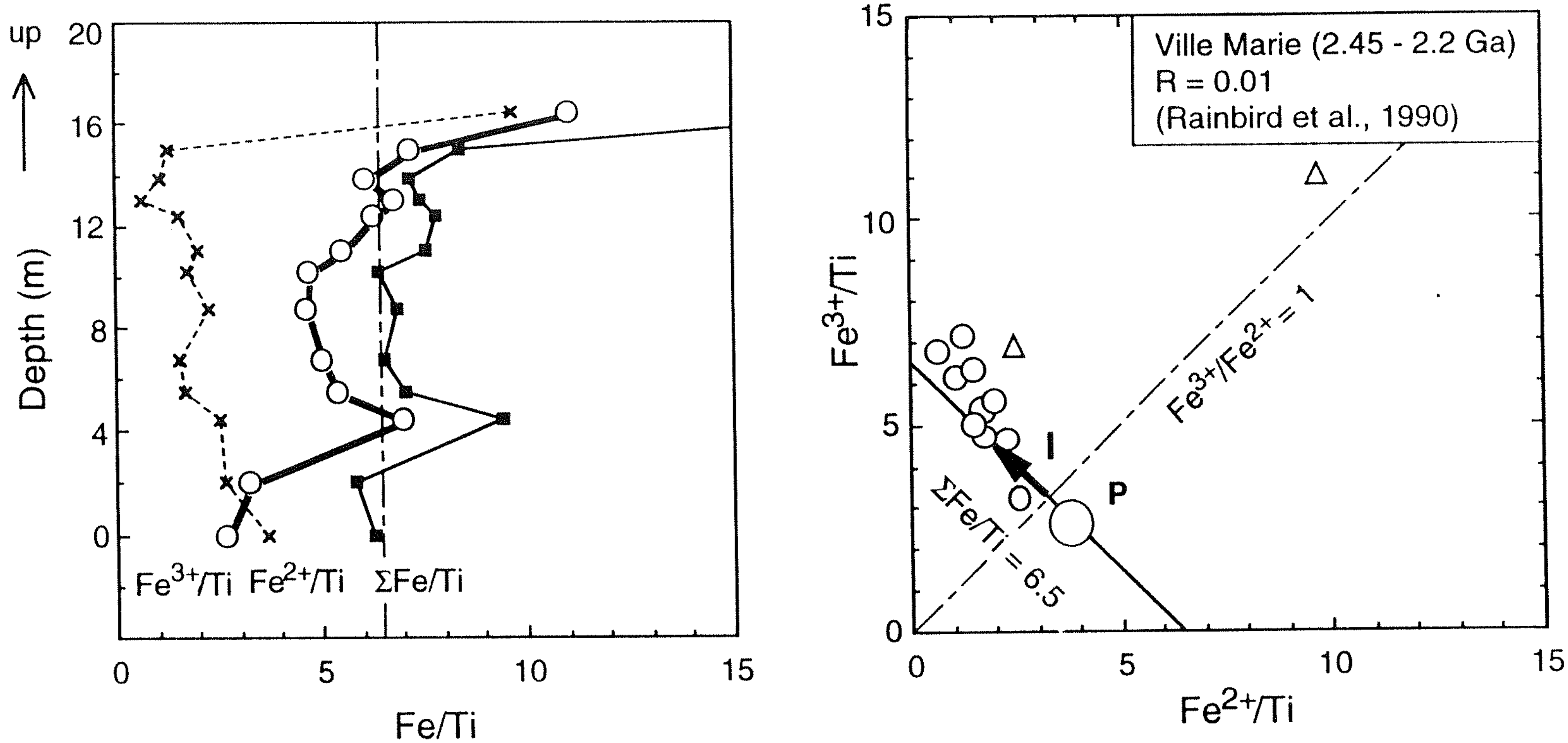

up
Sample No.
Fe3+/Ti
Fe2+/Ti
ΣFe/Ti
Fe/Ti
Fe3+/Ti
Fe2+/Ti
Villebon (2.75 Ga)
R = 0.02
(Vogel, 1975)
ΣFe/Ti = 11
Fe3+/Fe2+ = 1
P



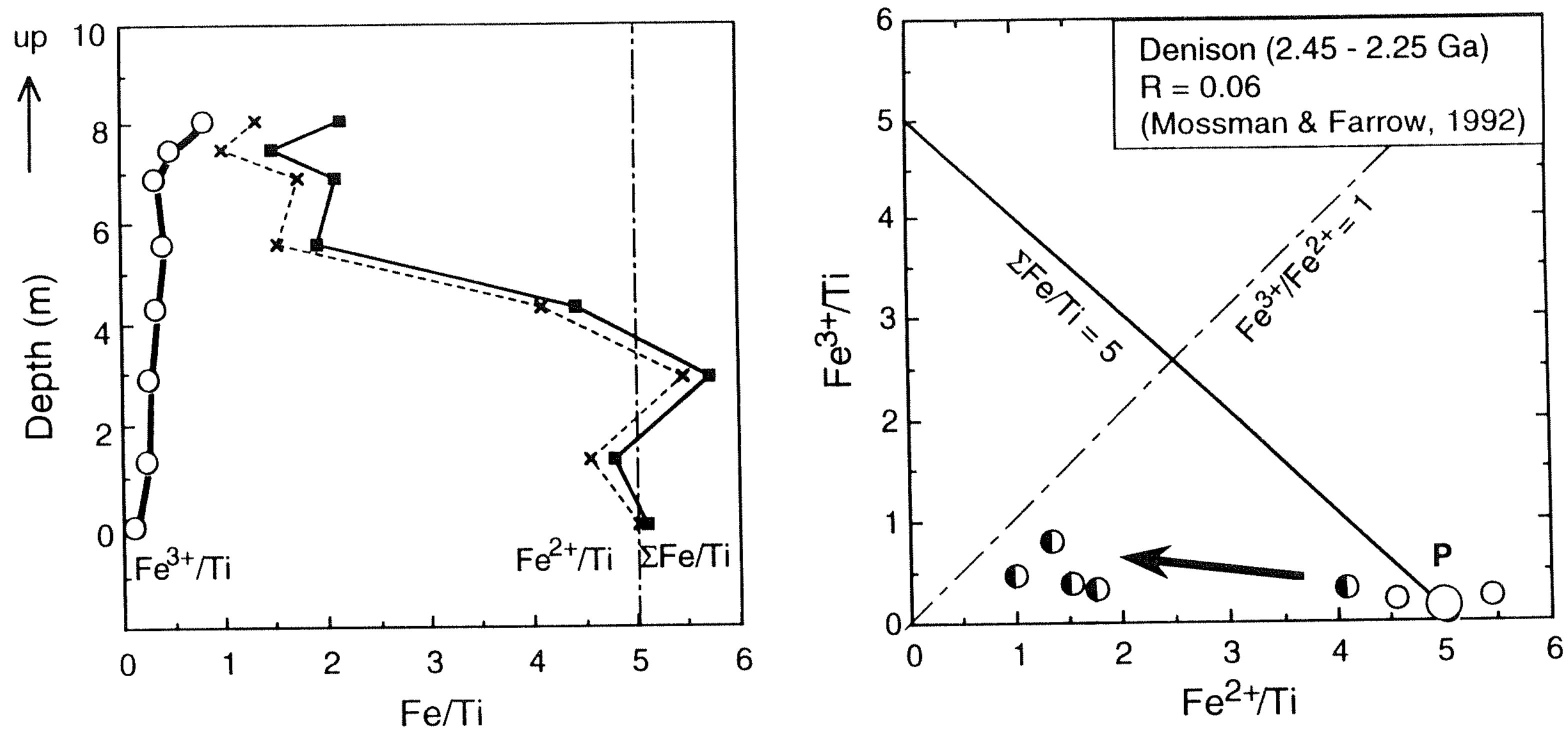
up
Depth (m)
Fe/Ti
ΣFe/Ti
Fe3+/Ti
Fe2+/Ti
Mt. Roe (2.75 Ga)
R = 0.02
(Macfarlane et al., 1994)
Fe3+/Fe2+ = 1
ΣFe/Ti = 7.5
P?
III
△?

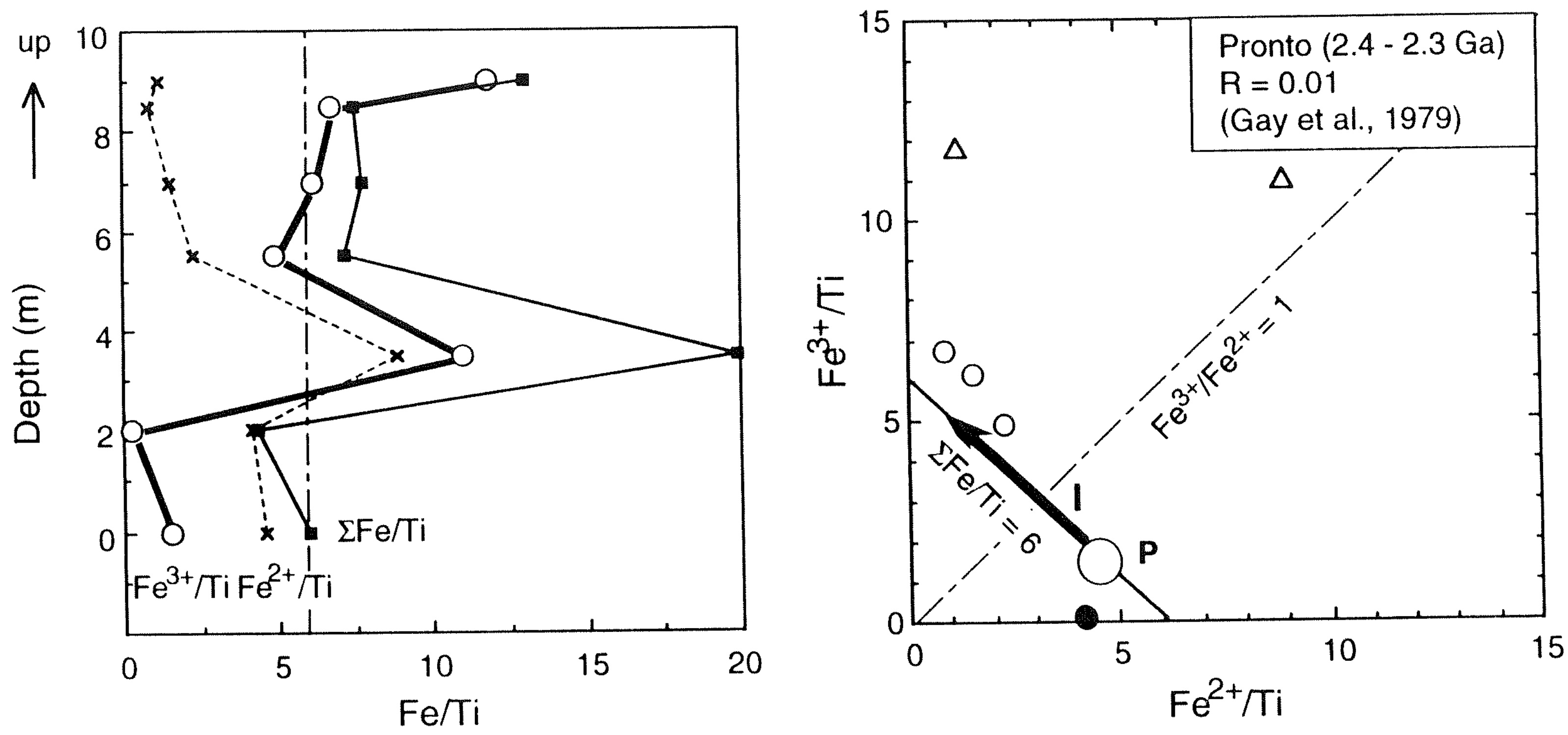


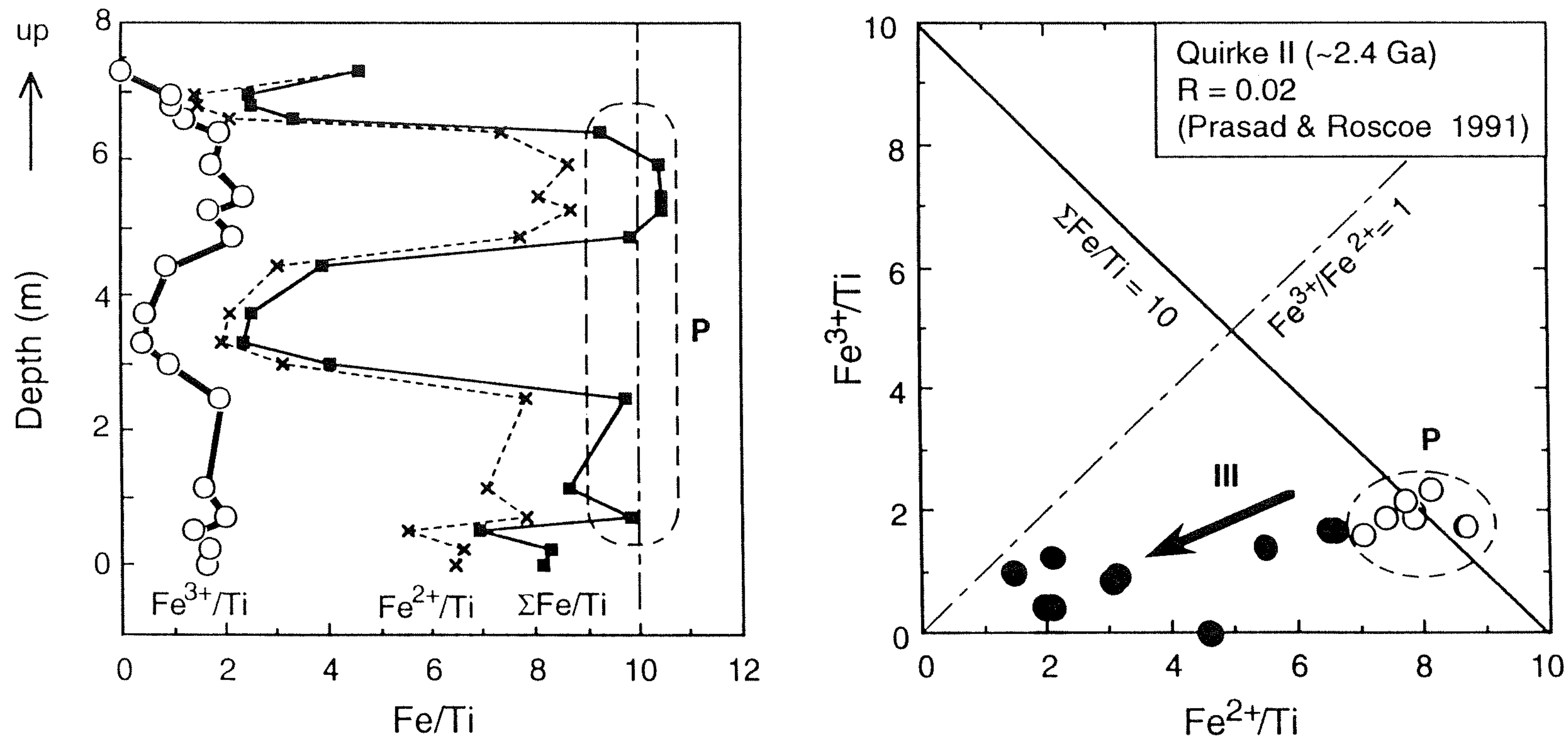
up
Depth (m)
Fe/Ti
Fe3+/Ti
Fe2+/Ti
ΣFe/Ti
Hokkalampi (2.5 - 2.2 Ga)
R = 0.03
(Marmo, 1992)
ΣFe/Ti = 10.5
Fe3+/Fe2+ = 1
I
II
P
Fe3+/Ti
Fe2+/Ti

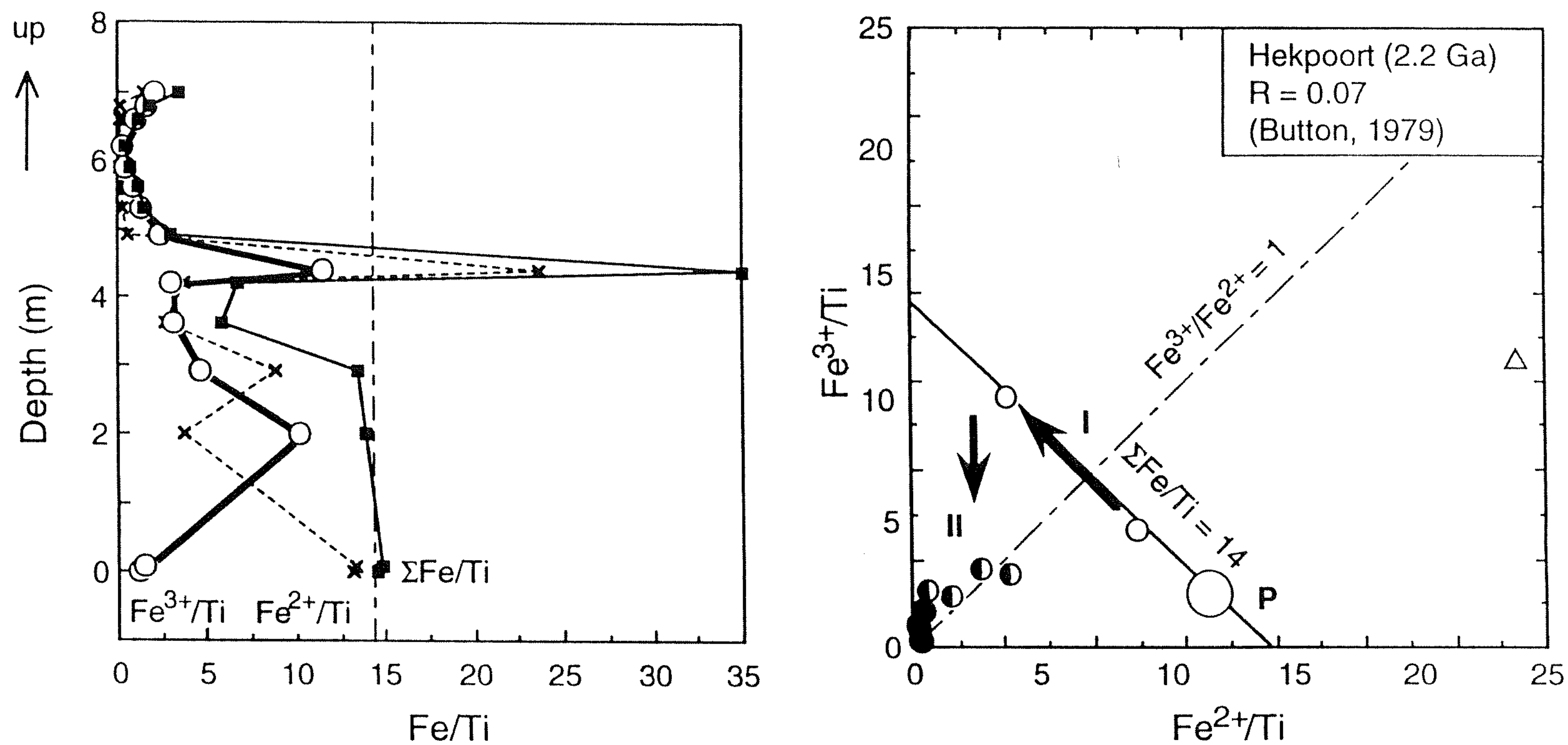


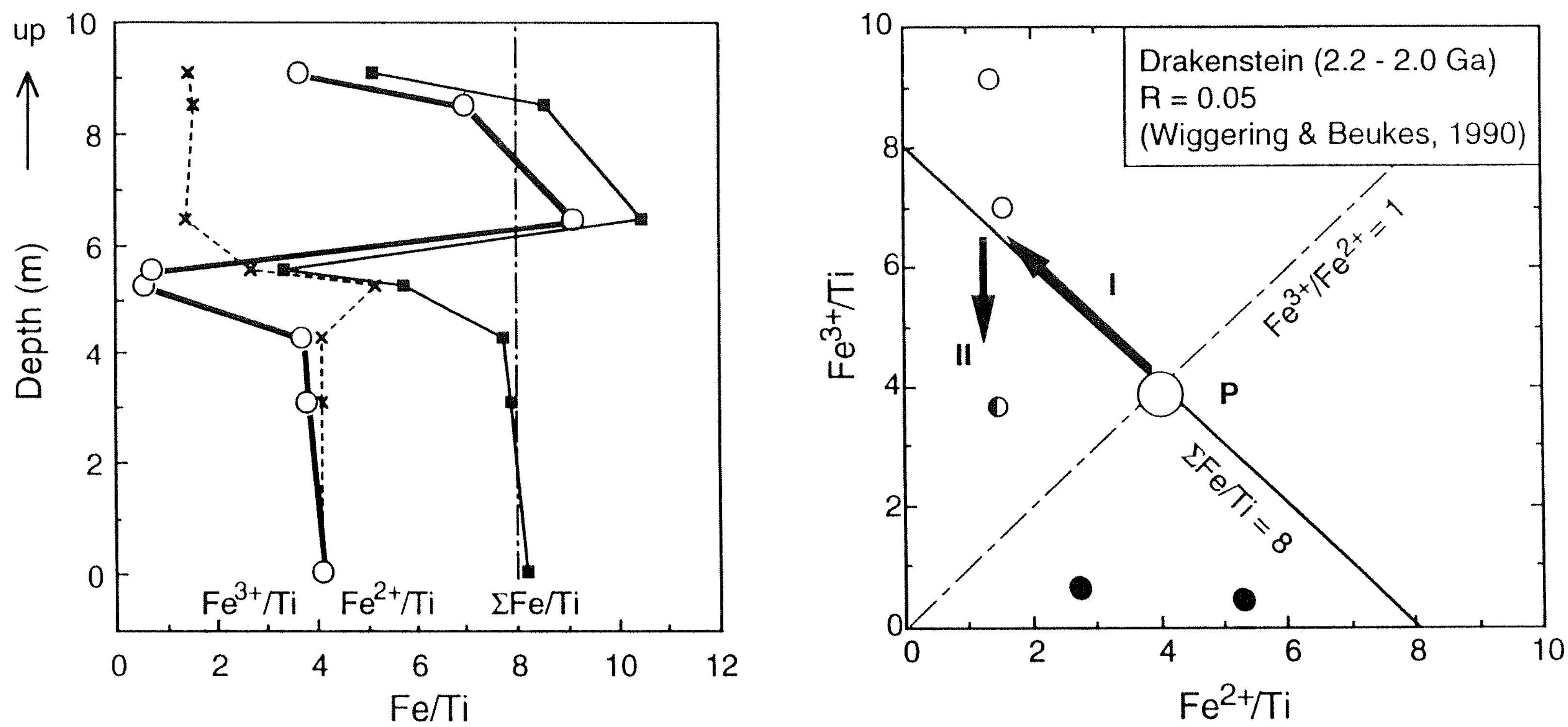
up
Depth (m)
Fe^3+/Ti Fe^2+/Ti ΣFe/Ti
Fe/Ti
Ville Marie (2.45 - 2.2 Ga)
R = 0.01
(Rainbird et al., 1990)
Fe^3+/Ti
Fe^2+/Ti
Fe^3+/Fe^2+ = 1
ΣFe/Ti = 6.5
I
P

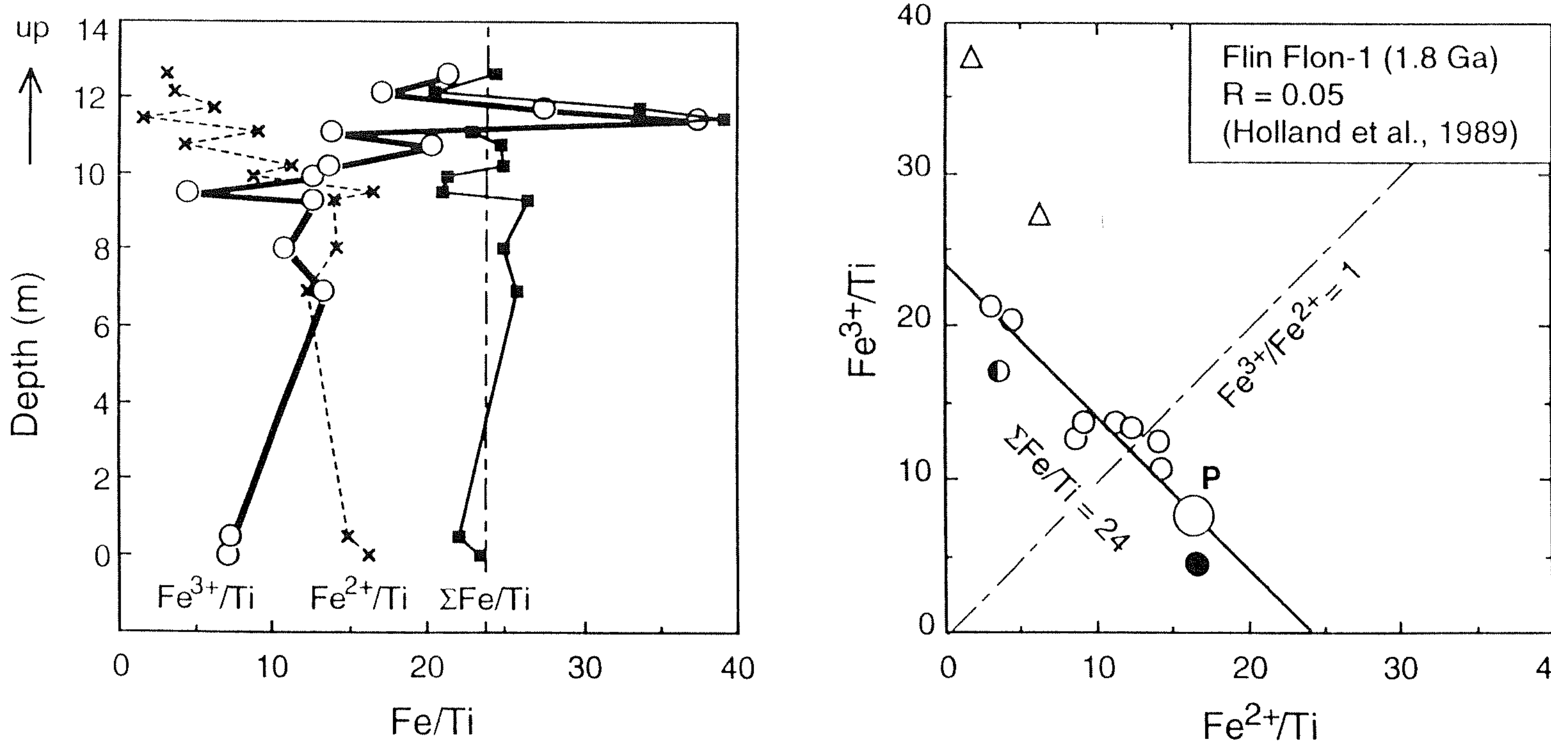

up
Depth (m)
Fe/Ti
Fe3+/Ti
Fe2+/Ti
ΣFe/Ti
Denison (2.45 - 2.25 Ga)
R = 0.06
(Mossman & Farrow, 1992)
ΣFe/Ti = 5
Fe3+/Fe2+ = 1
P
Fe3+/Ti
Fe2+/Ti


up
Depth (m)
Fe/Ti
ΣFe/Ti
Fe3+/Ti Fe2+/Ti
Pronto (2.4 - 2.3 Ga)
R = 0.01
(Gay et al., 1979)
Fe3+/Ti
Fe2+/Ti
Fe3+/Fe2+ = 1
ΣFe/Ti = 6
I
P

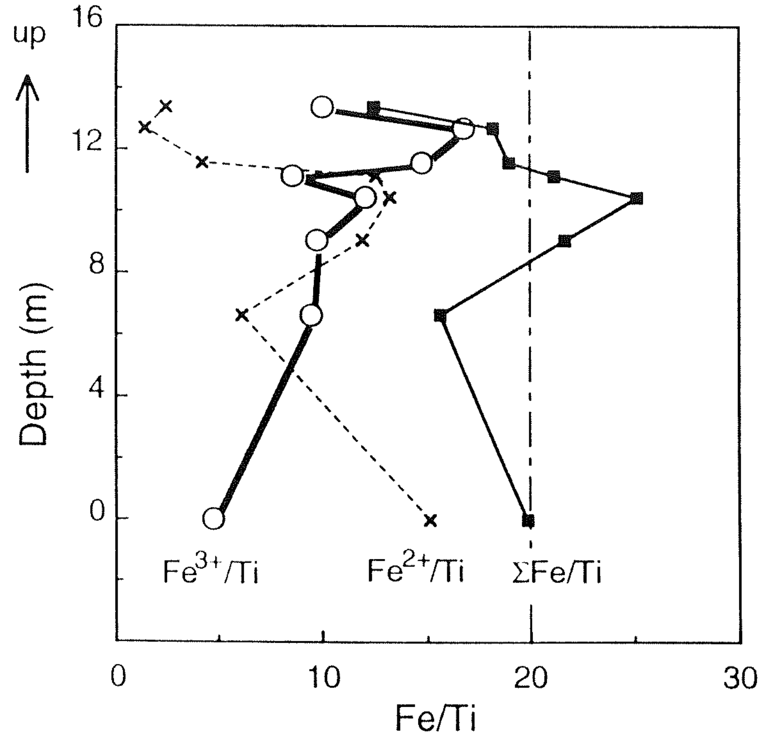

up
Depth (m)
Fe/Ti
Fe3+/Ti
Fe2+/Ti
ΣFe/Ti
P
Quirke II (~2.4 Ga)
R = 0.02
(Prasad & Roscoe 1991)
ΣFe/Ti = 10
Fe3+/Fe2+ = 1
III
Fe3+/Ti
Fe2+/Ti

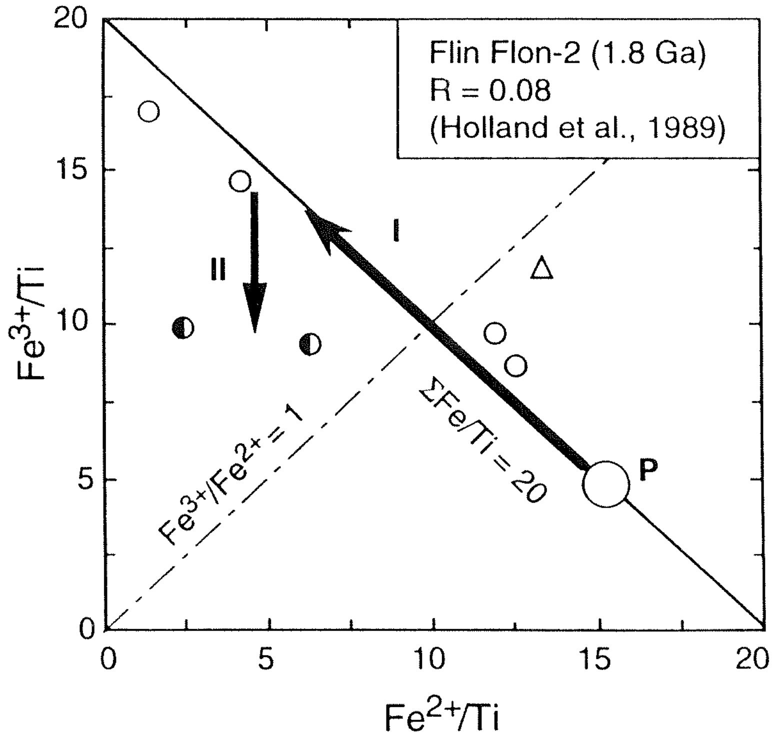

up
Depth (m)
Fe/Ti
Fe^{3+}/Ti
Fe^{2+}/Ti
$\Sigma Fe/Ti$
Hekpoort (2.2 Ga)
R = 0.07
(Button, 1979)
$Fe^{3+}/Fe^{2+} = 1$
$\Sigma Fe/Ti = 14$
I
II
P
Fe^{3+}/Ti
Fe^{2+}/Ti


up
Depth (m)
Fe/Ti
Fe^{3+}/Ti
Fe^{2+}/Ti
ΣFe/Ti
Drakenstein (2.2 - 2.0 Ga)
R = 0.05
(Wiggering & Beukes, 1990)
Fe^{3+}/Ti
Fe^{2+}/Ti
Fe^{3+}/Fe^{2+} = 1
ΣFe/Ti = 8
I
II
P

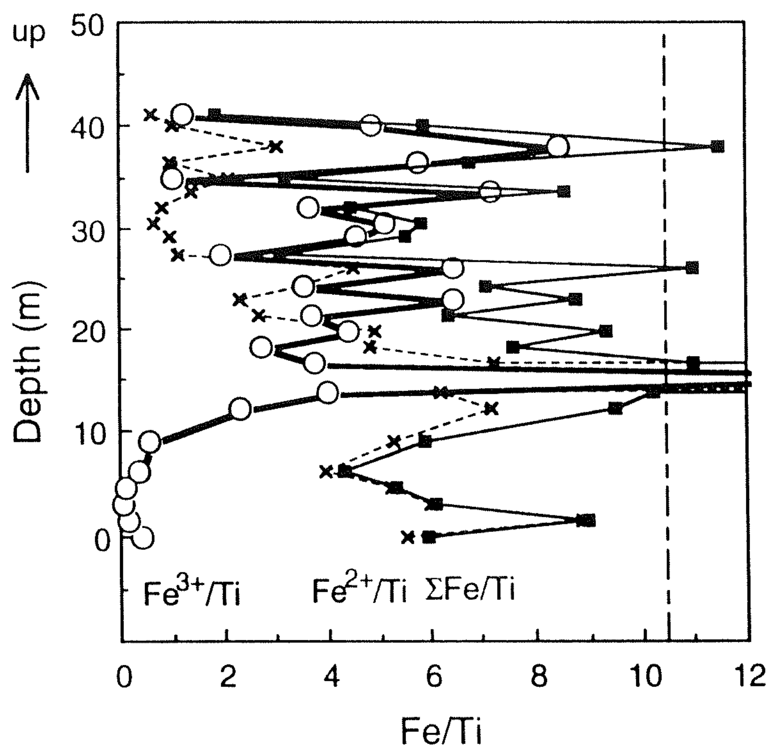


up
Depth (m)
Fe/Ti
Fe^{3+}/Ti
Fe^{2+}/Ti
$\Sigma Fe/Ti$
Flin Flon-1 (1.8 Ga)
R = 0.05
(Holland et al., 1989)
$Fe^{3+}/Fe^{2+} = 1$
$\Sigma Fe/Ti = 24$
P
Fe^{3+}/Ti
Fe^{2+}/Ti

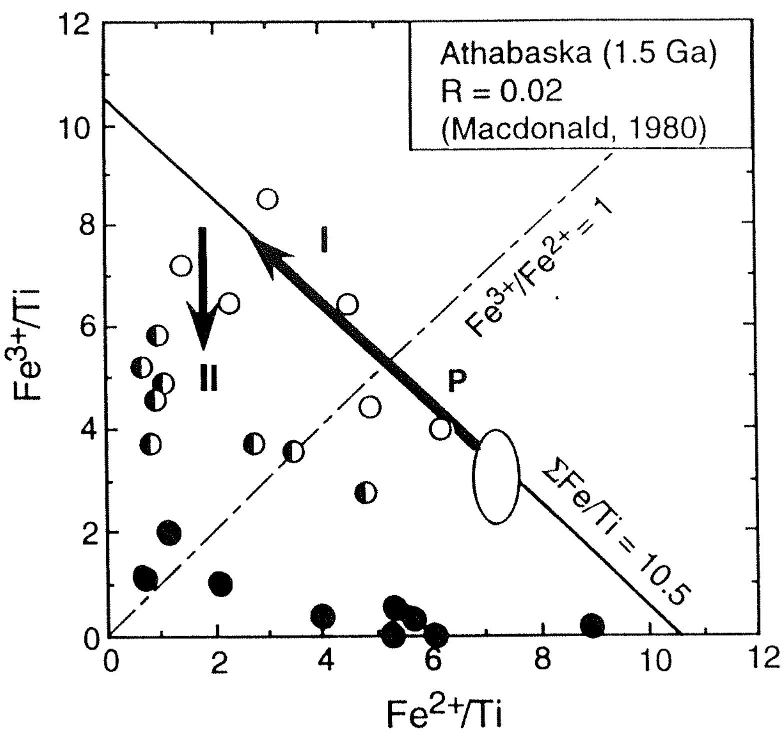

up
Depth (m)
16
12
8
4
0
Fe3+/Ti
Fe2+/Ti
ΣFe/Ti
0
10
20
30
Fe/Ti


Flin Flon-2 (1.8 Ga)
R = 0.08
(Holland et al., 1989)
I
II
P
ΣFe/Ti = 20
Fe3+/Fe2+ = 1
Fe3+/Ti
Fe2+/Ti
0
5
10
15
20

(Hole 20)

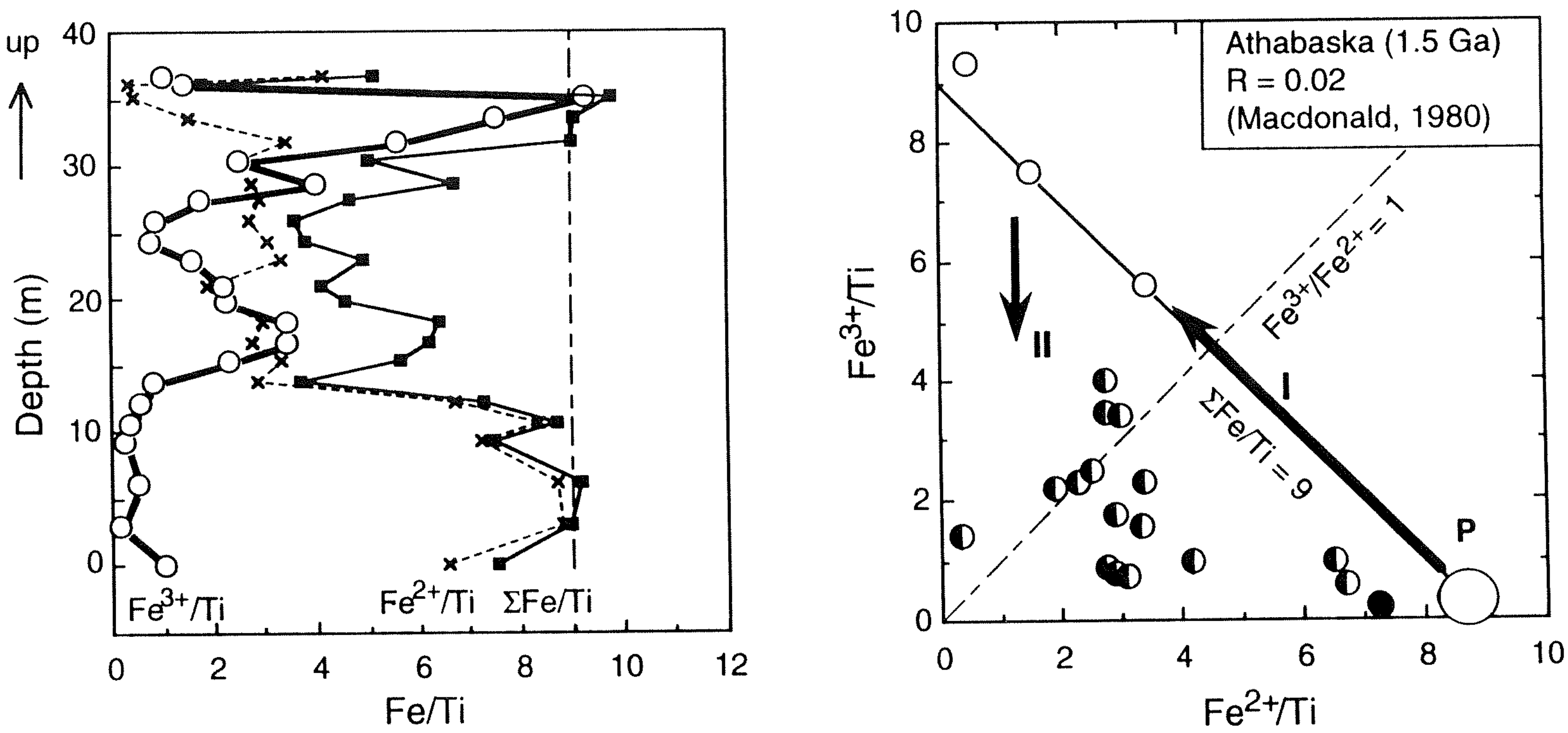


up
Depth (m)
Fe/Ti
Fe3+/Ti
Fe2+/Ti
ΣFe/Ti

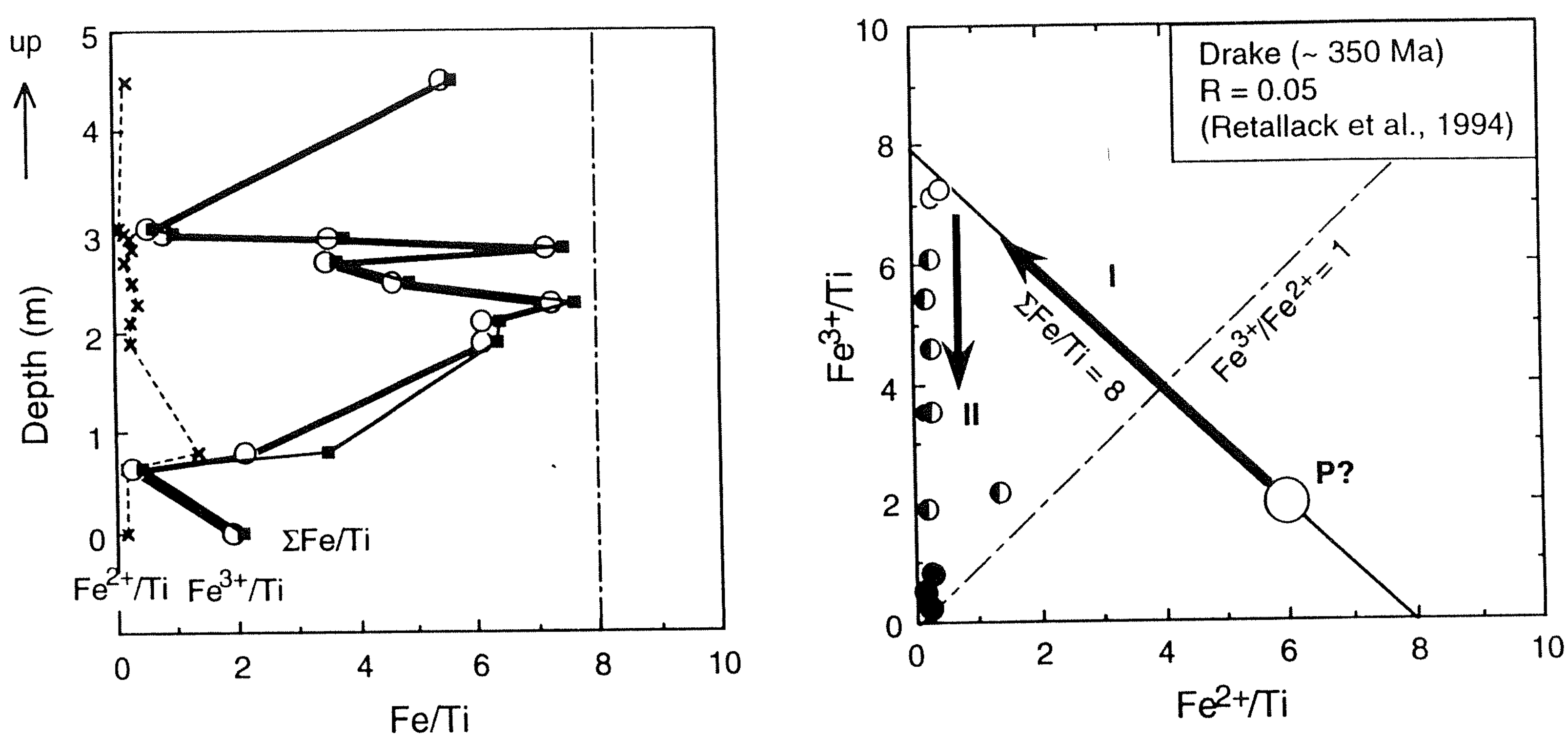


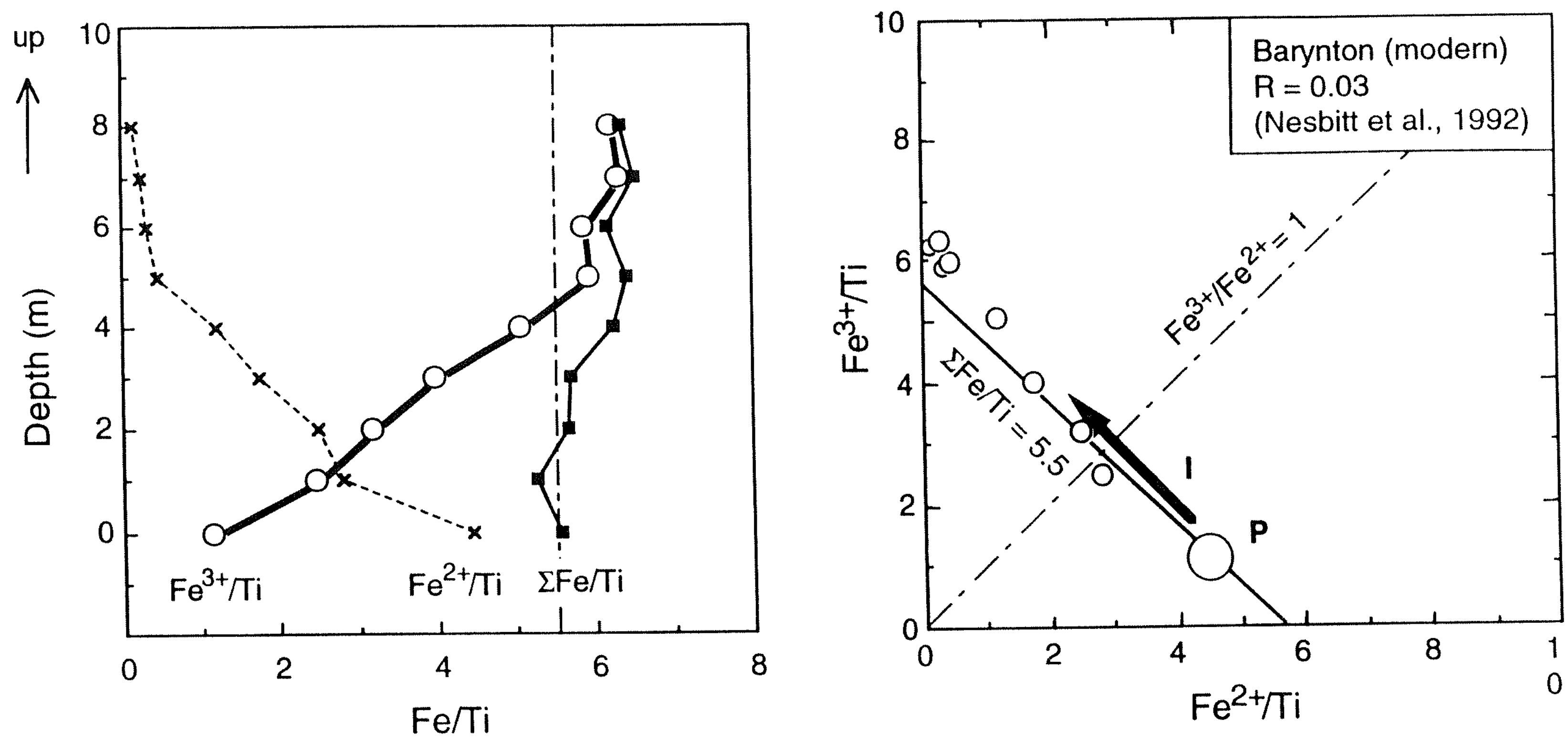
Athabaska (1.5 Ga)
R = 0.02
(Macdonald, 1980)
Fe3+/Ti
Fe2+/Ti
Fe3+/Fe2+ = 1
ΣFe/Ti = 10.5
I
II
P

(Hole 81)



up
Depth (m)
Fe/Ti
Fe^{3+}/Ti
Fe^{2+}/Ti
$\Sigma Fe/Ti$
Athabaska (1.5 Ga)
R = 0.02
(Macdonald, 1980)
$Fe^{3+}/Fe^{2+} = 1$
$\Sigma Fe/Ti = 9$
I
II
P
Fe^{3+}/Ti
Fe^{2+}/Ti


up
Depth (m)
Fe/Ti
Fe2+/Ti
Fe3+/Ti
ΣFe/Ti
Drake (~ 350 Ma)
R = 0.05
(Retallack et al., 1994)
Fe3+/Ti
Fe2+/Ti
ΣFe/Ti = 8
Fe3+/Fe2+ = 1
I
II
P?



up
Depth (m)
Fe/Ti
Fe^{3+}/Ti
Fe^{2+}/Ti
ΣFe/Ti
Barynton (modern)
R = 0.03
(Nesbitt et al., 1992)
Fe^{3+}/Ti
Fe^{2+}/Ti
ΣFe/Ti = 5.5
Fe^{3+}/Fe^{2+} = 1
I
P