

REDOX HISTORY OF THE EARTH'S INTERIOR SINCE ~3900 Ma: IMPLICATIONS FOR PREBIOTIC MOLECULES

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*'The gossamer web of life, spun on the
loom of sunlight from the breath of an
infant Earth, is Nature's crowning
achievement on this planet'.*

Cloud (1988)

Abstract. The history of the oxidation state in the Earth's mantle has been constrained using (a) the whole-rock abundances of Cr and V in ancient volcanics, and (b) the composition of Cr-rich spinels in ancient volcanics. Results indicate that the Earth's mantle has been at-or-near its current oxidation state (± 0.5 log-unit fO_2) since at least 3600 Ma, and probably since at least 3960 Ma. Volatiles released into the Earth's atmosphere by high-temperature ($T \geq 1300$ K) volcanism during this time have been dominated by H_2O , CO_2 , and SO_2 . This blend of volatiles is known to provide smaller yields of prebiotic, organic molecules by atmospheric and surface processes than gas mixtures containing higher concentrations of reduced species such as H_2 , CO, and H_2S (e.g., Miller, 1998; Zolotov and Shock, 2000). The results discussed in this article independently support the conclusion of Canil (1997, 1999). **If** the atmosphere was reducing (e.g., CH_4 , H_2 , H_2S , NH_3 , CO) at any time during the last ~3900 Ma, high-temperature volcanic outgassing was not the cause of it.

Keywords: basaltic volcanism, chromium, oxidation state, reducing atmosphere, spinel, volcanic gases

1. Introduction

Although the time of life's origin on Earth is currently uncertain, it is known to have occurred at >3500 Ma (Schopf, 1993, 1999), and probably at >3800 Ma (Mojzsis *et al.*, 1996). The environmental insults (e.g., sterilizing impacts) that determined when life on Earth first became sustainable (in a variety of potential settings) range from ~3800–4000 Ma (e.g., Maher and Stevenson, 1988; Oberbeck and Fogleman, 1990; Sleep and Zahnle, 1998; Zahnle and Sleep, 1996), ~4000–4200 Ma (e.g., Sleep *et al.*, 1989), and perhaps ~4400 Ma (Mojzsis *et al.*, 2001; Sleep *et al.*, 2001; Wilde *et al.*, 2001).



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The composition of the Earth's early atmosphere has figured importantly in discussions on the possible source of prebiotic molecules that might have led to the origin of life (e.g., Miller, 1953; Oparin, 1938). Possible sources of prebiotic molecules that led to the origin of life on Earth include interplanetary dust particles (e.g., Maurette, 1998), comets (e.g., Chyba, 1990; Chyba and Sagan, 1992; Delsemme, 1998; Kasting, 1990; Oro, 1961), high-temperature volcanic outgassing (e.g., Kasting *et al.*, 1993; Kasting and Brown, 1998; Navarro-Gonzalez *et al.*, 1998; Zolotov and Shock, 2000), and hydrothermal vents (e.g., Cody *et al.*, 2000; Holm, 1990; Holm and Andersson, 1998; Shock, 1990; Shock *et al.*, 1999; Schoonen *et al.*, 1999; Wachtershauser, 1990). For the case of high-temperature volcanic outgassing, the oxidation state of the Earth's mantle would have determined the composition of gases released. At the current oxidation state of the Earth's mantle, which is approximated by the fayalite-magnetite-quartz (FMQ) buffer (e.g., Blundy *et al.*, 1991; Bryndzia and Wood, 1990; Buddington and Lindsley, 1964; Carmichael *et al.*, 1974; Christie *et al.*, 1986; Eggler, 1983; Gerlach, 1980; Gurenko and Schmincke, 2000; Haggerty, 1978; Sato and Wright, 1966; Symonds *et al.*, 1994), the gases released by high-temperature (e.g., ~ 1300 K) volcanic eruptions are dominated by H_2O , CO_2 , and SO_2 with smaller abundances ($\leq 1\%$) of H_2 and CO (e.g., Zolotov and Shock, 2000). This composition of gases is known to produce smaller yields of prebiotic molecules than gas mixtures richer in H_2 , CO , H_2S , and other reduced molecules (e.g., Miller, 1998; Zolotov and Shock, 2000).

To assess the possible role of high-temperature volcanic outgassing as a potential source of the materials for making prebiotic molecules essential for the origin of life, the oxidation state of the Earth's interior must be known at the time when sustainable life originated. This topic has been discussed from many perspectives (e.g., Abelson, 1966; Holland, 1962, 1978, 1984; Kasting, 1993; Kasting *et al.*, 1993; Rubey, 1955; Walker, 1982, 1990). The current article has employed a different strategy than previous works in an attempt to constrain the history of the mantle's oxidation state, and hence the composition of volcanic gases released into the atmosphere through time by high-temperature volcanic eruptions.

Except for assessing the redox mechanism proposed by Kump *et al.* (2001), this article does not address the history of molecular oxygen abundances in the Earth's atmosphere (e.g., Karhu and Holland, 1996; Kasting, 1993; Murakami *et al.*, 2001; Ohmoto, 1996; Rye and Holland, 1998).

2. Methods

Published analyses of (a) fresh, mafic volcanics from mid-ocean ridges and Hawaii, and (b) Cr-rich spinels have been used, in conjunction with experimental data at 1-bar pressure, to define redox indicators for use on ancient volcanic samples. Although the Fe(III)/Fe(II) ratio is known to be a reliable indicator of oxidation state (e.g., Christie *et al.*, 1986), its use in whole-rock samples of ancient volcanics

as an indicator of the oxidation state of the Earth's mantle at the time of magma's eruption (e.g., Chang *et al.*, 1983; Holland, 1962) is potentially vulnerable to post-eruptive, redox alteration.

The original abundance of Cr in a volcanic whole-rock depends on the geochemical partitioning of Cr(II) and Cr(III) between crystalline solids (i.e., mantle residual minerals) and the melt at the time of its formation. Post-eruptive alteration of the rock's Cr(III)/Cr(II) ratio is largely irrelevant to the method applied in this article. As long as the rock's original whole-rock Cr abundance is not significantly changed (i.e., closed system to Cr loss/gain on the whole-rock scale), the redox memory remains intact. Chromium's low residence time in seawater (~1600 yr: Whitfield and Turner, 1979; Faure, 1998), which is similar to that of hafnium, is an indicator of the modest solubility of Cr(III) and Cr(VI) in the modern, aqueous solutions, and hence its modest mobility during alteration. Therefore, the whole-rock Cr-strategy described in this article relies on a more durable geochemical memory of ancient oxidation states in volcanic rocks than previous efforts that relied on the whole rock, Fe(III)/Fe(II) ratio.

2.1. GEOCHEMISTRY OF CHROMIUM (Cr)

Cr is a transition element that can occur in different valence states {Cr(II) and Cr(III)} within the range of redox conditions known to occur inside the mantles and crusts of terrestrial-type objects (i.e., Earth, Moon, Mars, and meteorite parent bodies), and as Cr(VI) in oxidative weathering environments. Cr(II) and Cr(III) have different behaviors during partial melting and fractional crystallization processes (e.g., Barnes, 1986; Hanson and Jones, 1998; Murck and Campbell, 1986; Roeder and Reynolds, 1991; Schreiber and Haskin, 1976). As an 'essential structural constituent' of an important accessory phase (i.e., Cr-rich spinel) in planetary mantles, the abundance of Cr in spinel-saturated, mafic magmas is controlled by temperature, pressure, bulk composition, and oxidation state of the magma (e.g., Barnes, 1986; Hanson and Jones, 1998; Hill and Roeder, 1974; Murck and Campbell, 1986; Roeder and Reynolds, 1991). The latter determines the Cr(III)/Cr(II) ratio of the system, and hence the geochemical behavior of Cr during melting and fractional crystallization (e.g., Schreiber and Haskin, 1976). Figure 1a illustrates this redox-sensitive behavior of Cr in a mafic melt (low-Ti, lunar picritic basalt) saturated with Cr-rich spinel (+ olivine) at constant temperature (1260 °C), 1-bar pressure, and constant bulk composition (total Cr = 4040 ppm) for a range of oxygen fugacities (FMQ = fayalite-magnetite-quartz buffer; IW = iron-wustite buffer). In these experiments, the ratio of crystals to melt is controlled by the constant temperature and the bulk composition of the system. The analytical uncertainties are ± 0.02 log-unit fO_2 and ± 100 ppm Cr. Figure 1a shows that the abundance of Cr in this mafic melt at spinel (+olivine) saturation is low at oxidizing conditions (FMQ) and increases systematically with decreasing oxygen fugacity (IW).

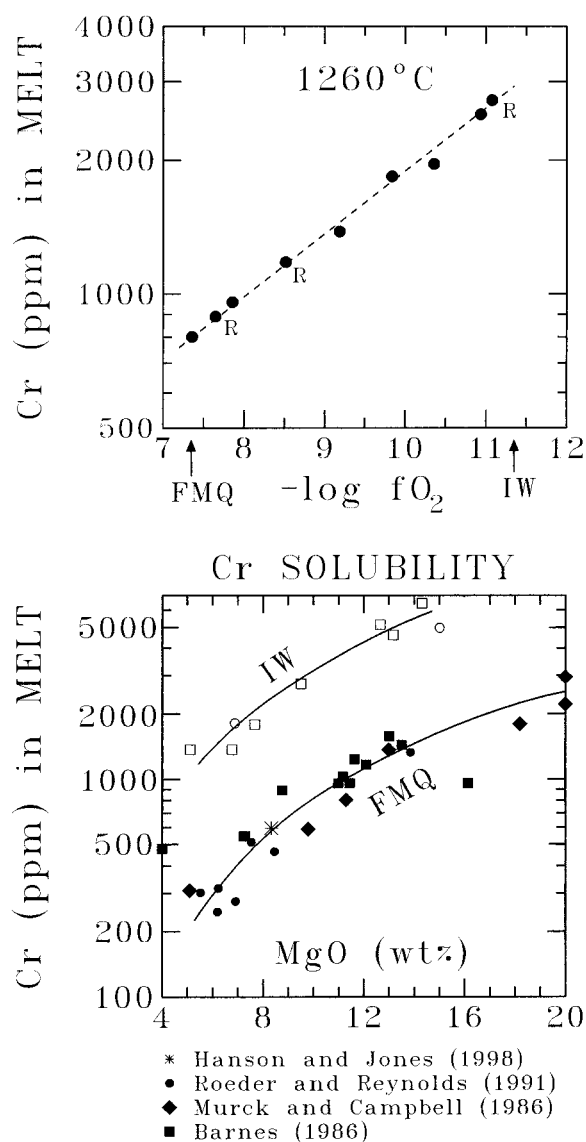


Figure 1a-b. (a) Experimental results showing Cr-solubility in a spinel+olivine saturated, basaltic melt at constant temperature (1260 °C) and constant bulk composition (Apollo 15 lunar picritic glass with 4040 ppm Cr and liquidus temperature of ~1340 °C) as a function of oxygen fugacity. Each point is a single experiment that was run at the oxygen fugacity indicated and quenched. The three points with 'R' adjacent to them are experiments having deliberately complex histories in order to test that equilibrium had been achieved. Analytical uncertainties are ± 100 ppm Cr; ± 0.02 log-unit fO_2). FMQ = fayalite-magnetite-quartz buffer; IW = iron-wustite buffer. (b) Experimentally determined Cr-abundances in melts at spinel (+ Fe-Mg silicate, such as olivine and/or pyroxene) saturation for terrestrial magmatic compositions (Barnes, 1986; Hanson and Jones, 1998; Murck and Campbell, 1986; Roeder and Reynolds, 1991). The abundance of MgO in the melt is a proxy for temperature of equilibration. The two curves are fits to the data for reducing (IW; iron-wustite buffer; open boxes) and oxidizing (FMQ; fayalite-magnetite-quartz; solid boxes) conditions.

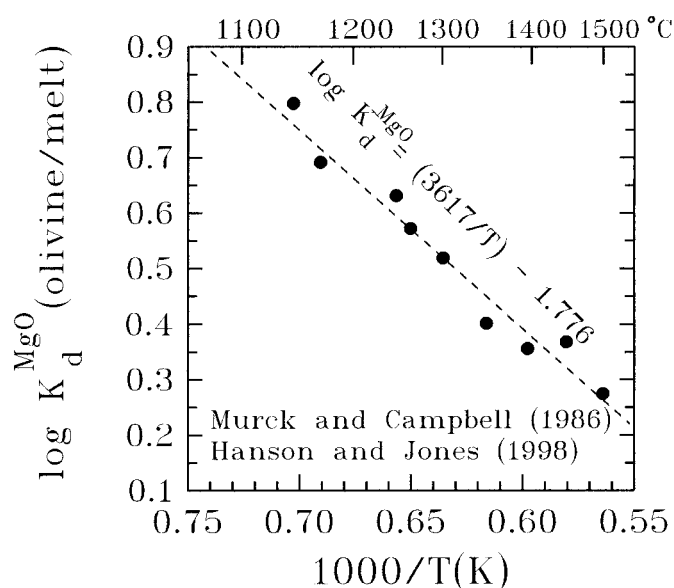


Figure 1c. (c) The temperature-dependence of MgO-partitioning is illustrated using the ratio of the mole fractions of MgO between olivine and the coexisting melt. This temperature-dependence is important in the approach described in this article (i.e., MgO vs Cr in ancient magmas). These experimental data on terrestrial compositions are from Hanson and Jones (1998) and Murck and Campbell (1986). The linear correlation coefficient, r , has a value of 0.982 for the equation listed. Refer to Ford *et al.* (1983) for more information.

Each point (Figure 1a) is a single experiment that involved a 500 mg, synthetic sample suspended on a Fe-doped Pt-wire (0.25-mm diameter) in a CO + CO₂ gas flow to obtain and maintain the desired oxygen fugacity. The temperature and oxygen fugacity of each experiment were continuously monitored for the duration of each experiment (~50–100 hr). Each experiment was terminated by electrically cutting the Pt-wire causing the sample to fall into a pool of water resulting in a rapid (<1 sec) quench. The desired oxygen fugacity was maintained during the quenching process. The samples were sectioned, polished, and analyzed by electron microprobe. The measured Cr abundances in the spinel-saturated melt (i.e., glass) are plotted on the y-axis (Figure 1a). The three points in Figure 1a having 'R' adjacent to them are experiments that underwent deliberately complex fO₂ histories in order to test that chemical equilibrium had been achieved among all of the experiments. For example, an experiment would initially be equilibrated in the furnace at one oxygen fugacity, but then the oxygen fugacity would be deliberately changed to a different value, and the sample would be held at those new conditions until quenched. If equilibration at the second set of conditions had occurred, then the abundance of Cr measured in the melt would agree with results from other experiments having simple run-histories. The agreement among these experiments in Figure 1a demonstrate that equilibration was achieved, and illustrate the geo-

chemical behavior of Cr over a range of Cr(III)/Cr(II) ratios existing between the FMQ buffer {Cr(III)-dominated system; Schreiber and Haskin, 1976} and IW buffer {Cr(II)-dominated system; Schreiber and Haskin, 1976}. The importance of Figure 1a is that it shows, in agreement with previous workers (e.g., Barnes, 1986; Hanson and Jones, 1998; Hill and Roeder, 1974; Murck and Campbell, 1986; Roeder and Reynolds, 1991), that partial melting of an oxidized (\sim FMQ) planetary mantle generates magmas (saturated with spinel \pm other phases) containing lower abundances of Cr than magmas produced by partial melting under reducing (\sim IW) conditions. These experimental data are available on request from the author.

Published experimental results on Cr-solubility in melts at spinel + olivine (and/or pyroxene) saturation for a range of terrestrial mafic compositions at FMQ (solid symbols) and IW (open symbols) conditions are plotted in Figure 1b (Barnes, 1986; Hanson and Jones, 1998; Murck and Campbell, 1986; Roeder and Reynolds, 1991). These data are for a range of temperatures (1150–1450 °C) and for a range of terrestrial bulk compositions (basalt to komatiite). As in the case of Figure 1a, the measured abundances of Cr in the melts (i.e., glass) coexisting with spinel + other phases are plotted along the y-axis. The x-axis shows the abundance of MgO (wt%) in the coexisting melts (Figure 1b). MgO serves as a proxy for the temperature at which chemical equilibration occurred between (i) the melt and (ii) the coexisting spinel + other phases. Specifically, high abundances of MgO in the melt indicate high temperatures (e.g., MgO = 20 wt% at 1450 °C: Murck and Campbell, 1986), whereas low abundances of MgO in the melt occur at low temperatures (e.g., MgO = 5.1 wt% at 1166 °C: Barnes, 1986). Further demonstration of the temperature-sensitivity of MgO in mafic systems is illustrated in Figure 1c where the ratio of mole fractions MgO in coexisting pairs of olivine and melts are plotted (Hanson and Jones, 1998; Murck and Campbell, 1986). This temperature-sensitive behavior of MgO is well-known (e.g., Ford *et al.*, 1983).

The summary of Cr-solubilities for terrestrial mafic compositions (Figure 1b) at FMQ and IW conditions is an important diagram. As a demonstration of its reliability when applied to natural systems, compositions of (i) basaltic glasses from mid-ocean ridges, (ii) Hawaiian volcanics, and (iii) lunar basalts and picritic glasses have been plotted in Figures 2a,b. These choices of compositions have been made for two reasons. First, all of these geologically young samples are fresh, and therefore retain the bulk compositions (for the elements of interest in this study) since the time of their eruptions. Second, since the oxidation states of these volcanic samples are independently known, the reliability of the calibration summarized in Figure 1b can be tested. The oxidation states of modern/recent eruptives on Earth (i.e., mid-ocean ridge basalts, MORB, and Hawaiian volcanics) are known to be near the FMQ buffer (e.g., Carmichael *et al.*, 1974; Christie *et al.*, 1986; Gurenko and Schmincke, 2000; Haggerty, 1978; Sato and Wright, 1966; Symonds *et al.*, 1994), whereas lunar volcanics are known to be slightly more reduced than the IW buffer (e.g., Smith *et al.*, 1970). Inspection of Figure 2a shows that the 295 MORB glasses (open circles) plot at MgO and Cr abundances indicating that they

were formed at redox conditions similar to, or slightly more oxidizing than, the FMQ buffer. As noted previously, this is broadly consistent with what is known about the oxidation state of modern volcanics coming from the Earth's mantle. Similarly, the 26 samples of basalts and picritic glasses from the Moon (half-filled circles) have MgO and Cr abundances consistent with their having formed at redox conditions similar to the IW buffer. As noted previously, this too is consistent with what is known about the Moon's mantle at the time of eruption of these magmas at 3300–3900 Ma. The compositions of 207 whole-rock volcanics from Hawaii (Figure 2b) indicate that these volcanics were formed near the FMQ buffer, which is again consistent with what is known about the present oxidation state of the Earth's mantle.

In summary, the experimentally defined systematics between MgO vs Cr (Figure 1b) have been used to independently estimate the known oxidation states of (i) modern eruptives on the Earth, and (ii) basalts and picritic glasses from the Moon (Figures 2a, b). These results are in broad agreement with other methods.

2.2. GEOCHEMISTRY OF VANADIUM (V)

Like Cr, V can also occur in different valence states {V(III), V(IV), and V(V)} within the range of redox conditions observed inside terrestrial planets (i.e., Earth, Moon, Mars, and meteorite parent bodies). The geochemical behaviors of these two species during partial melting and fractional crystallization are distinct (e.g., Canil, 1997, 1999; Shervais, 1982). As an illustration of this fact, and in association with the different behavior of Cr(III) and Cr(II) described previously, Figure 2c shows the different trends observed in (i) terrestrial volcanics (291 samples of MORB glasses and Hawaiian volcanics) and (ii) 18 lunar basalts and picritic glasses. Partial melting of the lunar and terrestrial mantles, although these mantles are thought to be similar in bulk composition (e.g., Wanke and Dreibus, 1986), produced magmas that differ significantly in their relative abundances and geochemical behaviors of Cr and V (Figure 2c). As expected, both sets of data trend toward the estimated upper mantle composition of Jagoutz *et al.* (1979) with increasing MgO (i.e., increasing percentages of partial melting).

In summary, Figure 2c shows that the behaviors of Cr and V during partial melting under oxidizing versus reducing conditions are readily distinguishable. This figure will also be used on suites of ancient terrestrial volcanics to estimate their original oxidation states at the time of eruption.

2.3. Fe(III)/Fe(II) RATIO IN Cr-RICH SPINELS

Cr-rich spinels are known to be useful petrogenetic indicators (e.g., Irvine, 1965). Published analyses of 307 Cr-rich spinels (Cr abundances range from ~20–47 wt% when calculated as Cr₂O₃) in MORB glasses (open circles) and Hawaiian volcanics (solid circles) are shown in Figure 3a. Since these spinels are from fresh samples, their original Fe(III)/Fe(II) ratios from the time of their crystallization in mafic

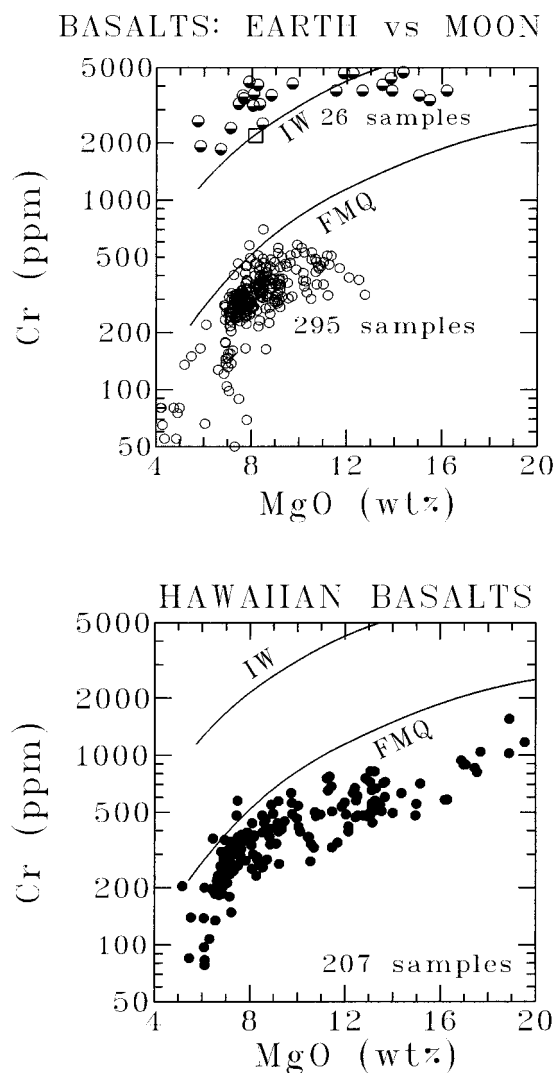


Figure 2a–b. (a) The abundances of MgO (wt%) and Cr (ppm) in 295 samples of (i) fresh, Mid-Ocean Ridge Basaltic (MORB) glasses and (ii) lunar basalts and picritic volcanic glasses are shown. The two curves labelled ‘IW’ and ‘FMQ’ are experimentally defined solubility curves at spinel (+Fe–Mg silicate) saturation from Figure 1b. Data for **MORB glasses** are from Allan *et al.* (1989), Bender *et al.* (1984), Bryan *et al.* (1981), Clague *et al.* (1981), Cousens *et al.* (1995), Davis and Clague (1987), Frey *et al.* (1980, 1993), Gaetani (1990), Klein *et al.* (1991), Langmuir *et al.* (1977), Muhe *et al.* (1997), Perfit *et al.* (1983), Rhodes *et al.* (1990), Shimizu (1998). Data for **lunar samples** are from Chappell and Green (1973), Compston *et al.* (1971), Delano (1986), Duncan *et al.* (1974), and Rhodes *et al.* (1974). Lunar data: half-filled circles are maria volcanics; open square is KREEP basalt, 15386. (b) Whole-rock abundances of MgO (wt%) and Cr (ppm) in 207 samples of recent Hawaiian volcanics. The two curves labelled ‘IW’ and ‘FMQ’ are experimentally defined solubility curves at spinel (+Fe–Mg silicate) saturation from Figure 1b. **Hawaiian data** are from Basaltic Volcanism Study Project (1981), Clague and Beeson (1980), Clague and Frey (1982), Rhodes (1983, 1988), Tilling *et al.* (1987), Wright (1971), and Wright and Peck (1978).

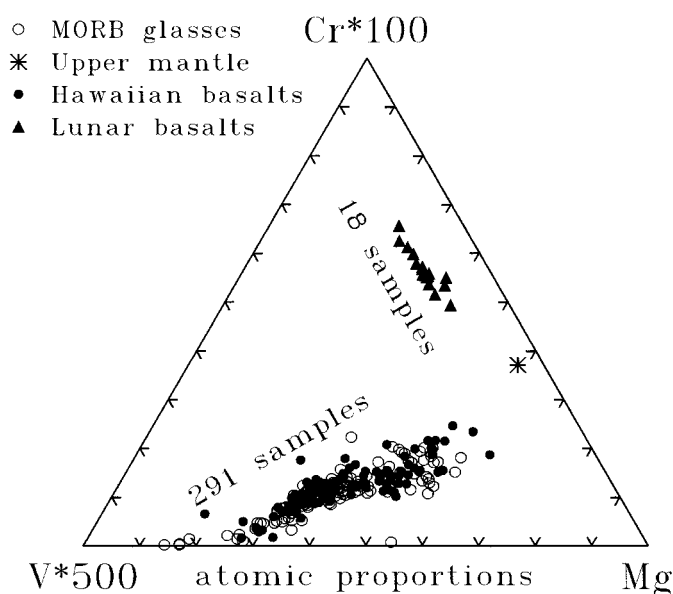


Figure 2c. (c) Ternary diagram showing the relative atomic abundances of Mg, Cr, and V in (i) MORB glasses, (ii) Hawaiian volcanics, (ii) lunar basalts and picritic glasses, and (iv) the Earth's upper mantle. Abundances of Cr and V have been amplified by large coefficients so that they have comparable weighting as the major element, Mg. Both Cr and V occur at different valence states in the Earth {~FMQ with Cr(III) and V(V)} and in the Moon {~IW with Cr(II) and V(III)}. These different valence states account for the strong differences evident in the compositions of the terrestrial and lunar volcanics shown, although the mantles of both the Earth and the Moon are thought to be broadly similar for these three elements (e.g., Dreibus and Wanke, 1986). Increased percentages of partial melting move compositions of magmas toward the upper mantle point. **Terrestrial data** are from Bender *et al.* (1984), Bryan *et al.* (1981), Constantin (1999), Cousens *et al.* (1995), Feigenson (1984), Gaetani (1990), Klein *et al.* (1991), Langmuir *et al.* (1977), Muhe *et al.* (1997), Perfit *et al.* (1983), Rhodes *et al.* (1990), Shimizu (1998), and Tilling *et al.* (1987). **Mantle composition** is from Jagoutz *et al.* (1979). **Lunar data** are from Compston *et al.* (1971), Cuttitta *et al.* (1973), Delano (1986), and Shearer and Papike (1993).

magmas are likely to have been retained, although re-equilibration can occur during both slow cooling and subsequent metamorphism (e.g., Scowen *et al.*, 1991; Ulmer, 1974). In contrast, Cr-rich spinels from lunar basalts (not shown) plot along the Mg–Fe(II) join of the ternary indicating no detectable Fe(III) in those phases, as expected under reducing conditions. Experimentally generated Cr-rich spinels equilibrated at the FMQ buffer (Figure 3b) generally plot within the field defined by the terrestrial spinels from Figure 3a.

Although Cr-rich spinels are chemically resistant phases under some conditions of terrestrial alteration and metamorphism, their geochemical memories are not likely to be as durable and reliable as the whole-rock approaches previously described in this article (i.e., Figures 1b, 2a–c). Nonetheless, under some circum-

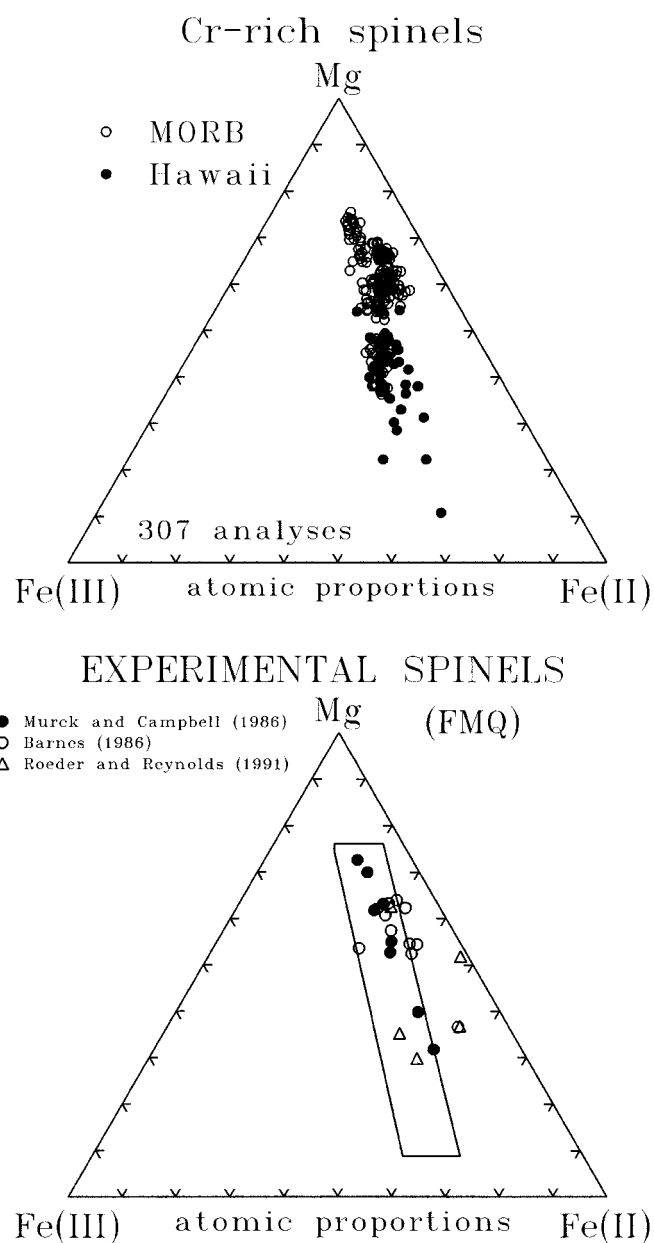


Figure 3a–b. (a) Atomic proportions of Mg, Fe(II), and Fe(III) in 307 Cr-rich spinels from unaltered Mid-Ocean Ridge Basalts (MORB: open circles) and unaltered Hawaiian volcanics (solid circles). Data are from Allan *et al.* (1988, 1989), Batiza and Vanko (1984), Bryan *et al.* (1981), Davis and Clague (1987), Evans and Wright (1972), Furuta and Tokuyama (1983), Gaetani (1990), Nicholls and Stout (1988), and Wilkinson and Hensel (1988). (b) Atomic proportions of Mg, Fe(II), and Fe(III) in experimentally produced, Cr-rich spinels at FMQ conditions compared with the field defined by natural Cr-rich spinels from MORB and Hawaiian samples from Figure 3a. Experimental data are from Barnes (1986), Murck and Campbell (1986), and Roeder and Reynolds (1991).

stances, this mineral may provide circumstantial evidence about original oxidation states of ancient terrestrial volcanics.

2.4. CRITERION FOR IDENTIFYING OPEN-SYSTEM ALTERATION

The goal of this study has been to use the geochemistry of ancient volcanic samples to place constraints on their oxidation states at the time of eruption. While Figures 2a–c form the basis for arguing that the whole-rock abundances in fresh samples provide reliable information about oxidation states, in general agreement with other independent methods, application to ancient volcanics depends on the ability to identify ancient samples that have not been subjected to significant open-system alteration since their eruption. Samples that have been significantly altered on the whole-rock scale since their eruption will have lost their original geochemical memories, and therefore cannot be used. The sole criterion that has been used in this study, although more restrictive criteria could have been employed, is shown in Figure 4 where 485 fresh samples of MORB glasses and Hawaiian volcanics have been plotted. Since MgO is a key-component in this strategy that is potentially mobile on a whole-rock scale during open-system chemical alteration, the field defined by the dashed line in Figure 4 enclosing modern eruptives will be used as the sole criterion for using, or not using, specific samples of ancient volcanics. Since Al_2O_3 has a lower solubility, and hence lower mobility, than MgO during most conditions of weathering and alteration, Al_2O_3 is likely to behave as a conserved element.

In the next section where the geochemical compositions of ancient volcanics are discussed, the field defined in Figure 4 will be used as the starting point. Samples that plot outside that field in Figures 5a, 6a, and 7a are interpreted as having been chemically altered, and therefore to have lost the geochemical memories required for this investigation. Consequently, those outliers were excluded from subsequent figures (e.g., Figures 5b, 6b, and 7b) where the original oxidation states were inferred. Therefore, all samples that plot within the dashed field in Figures 5a, 6a, and 7a were presumed to have retained a geochemical memory of their original compositions and were plotted in Figures 5b, 5c, 6b, 6c, and 7b.

3. Results

3.1. 2400–2900 Ma

Published analyses (normalized to 100% on a volatile-free basis) of volcanic samples in the 2400–2900 Ma age-interval have been used in this study from Ontario, Canada (Arndt, 1977; Arndt *et al.*, 1977; Arndt and Nesbitt, 1982; Barnes *et al.*, 1983; Canil, 1987; Cattell and Arndt, 1987; Fan and Kerrich, 1997; Stone *et al.*, 1995; Whitford and Arndt, 1978; Wyman, 1999), the Baltic Shield (Puchtel *et al.*, 1996; Vogel *et al.*, 1998), the Superior Province of Canada (Polat *et al.*, 1998, 1999;

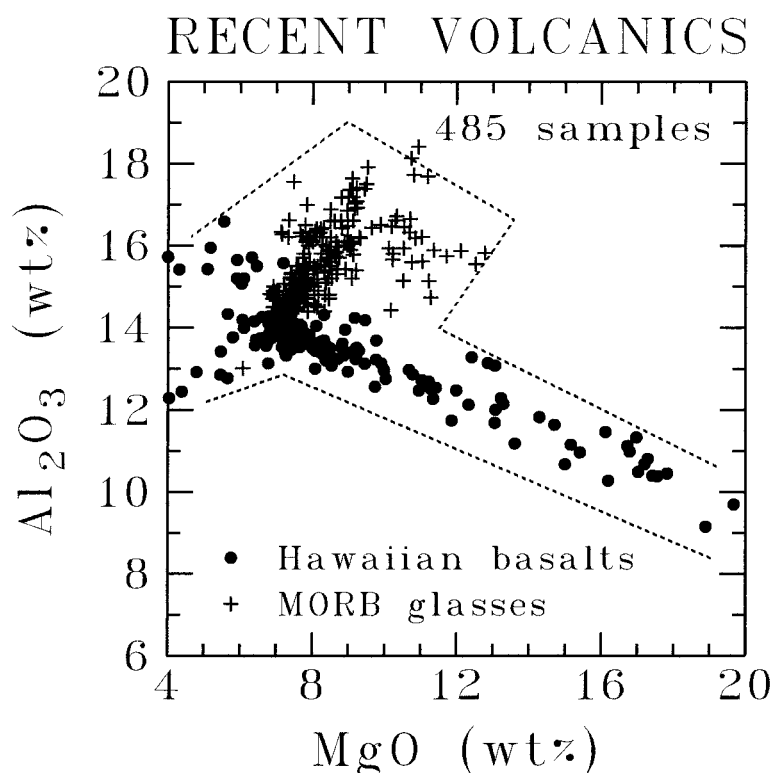


Figure 4. Measured abundances of MgO (wt%) and Al_2O_3 (wt%) in 485 samples of fresh MORB glass and Hawaiian volcanics. These data define the observed compositional characteristics of fresh (unaltered) volcanics that will be used as the sole selection criterion for ancient eruptives. The area defined by the dashed line, which is drawn around these fresh MORB glasses and Hawaiian volcanics, appears in subsequent figures as an assessment of 'degree of alteration'. **MORB data** are from sources listed in Figure 2a. **Hawaiian data** are from sources listed in Figure 2b.

Skulski *et al.*, 1988; Stern *et al.*, 1994), Rhodesia (Hawkesworth and O'Nions, 1977), Zimbabwe (Nisbet *et al.*, 1977, 1987; Wilson, 1982; Zhou and Kerrich, 1992), Western Australia (Barnes, 1998; Barnes and Hoatson, 1994; Nesbitt and Sun, 1976; Roeder and Campbell, 1985), South Africa (Crow and Condie, 1987, 1988), and India (Zachariah *et al.*, 1997). This geographically diverse set of 336 whole-rock samples are plotted on a volatile-free basis in Figure 5a relative to the field defined in Figure 4 by fresh, modern MORB glasses and Hawaiian volcanics. Forty (40) of the 336 samples that plot outside this field are interpreted as having been chemically altered on the whole-rock scale after their eruption and are excluded from subsequent figures. The 88% of 2400–2900 Ma samples (296) that plot within the field are interpreted as having retained their original compositions, and are subsequently used in Figures 5b, c. The open diamonds in Figure 5a are fresh, glass-bearing komatiitic lavas from the SASKMAR drill core near Belingwe,

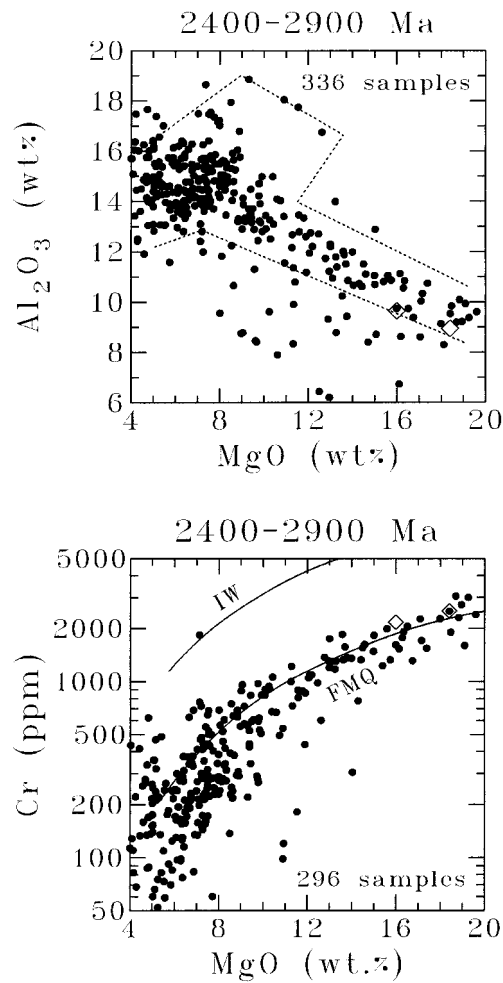


Figure 5a–b. (a) Whole-rock abundances (on a volatile-free basis) of MgO (wt%) and Al_2O_3 (wt%) in 336 volcanics having eruption ages of 2400–2900 Ma. The field defined by the dashed line is from Figure 4 showing the range of compositions among unaltered volcanics. Samples of 2400–2900 Ma volcanics that plot *outside this field* (40 samples) are interpreted as having been chemically altered after their formation and are not used in subsequent figures. 88% of the 336 samples that plot *within this field* (296 samples) are interpreted as having potentially retained their original compositions, and are used in Figures 5b and 5c. Data are from Arndt and Nesbitt (1976), Barnes *et al.* (1983), Canil (1987), Cattell and Arndt (1987), Crow and Condie (1987, 1988), Fan and Kerrich (1997), Hawkesworth and O’Nions (1977), Nesbitt *et al.* (1979), Nesbitt and Sun (1976), Polat *et al.* (1998, 1999), Puchtel *et al.* (1996), Skulski *et al.* (1988), Stern *et al.* (1994), Stone *et al.* (1995), Vogel *et al.* (1998), Whitford and Arndt (1978), Wilson (1982), Wyman (1999), and Zachariah *et al.* (1997). The **open diamonds** are fresh, glass-bearing, komatiitic basalts from the SASKMAR drill core in Belingwe, Zimbabwe (Nisbet *et al.*, 1987). (b) Whole-rock abundances (on a volatile-free basis) of MgO (wt%) and Cr (ppm) in 296 samples of 2400–2900 Ma volcanics that plotted *within the field* shown in Figure 5a. The open diamonds are fresh, glass-bearing komatiitic basalts from the SASKMAR drill core in Belingwe, Zimbabwe (Nisbet *et al.*, 1987). Nearly all of these samples are observed to plot near the FMQ line, as defined in Figure 1b.

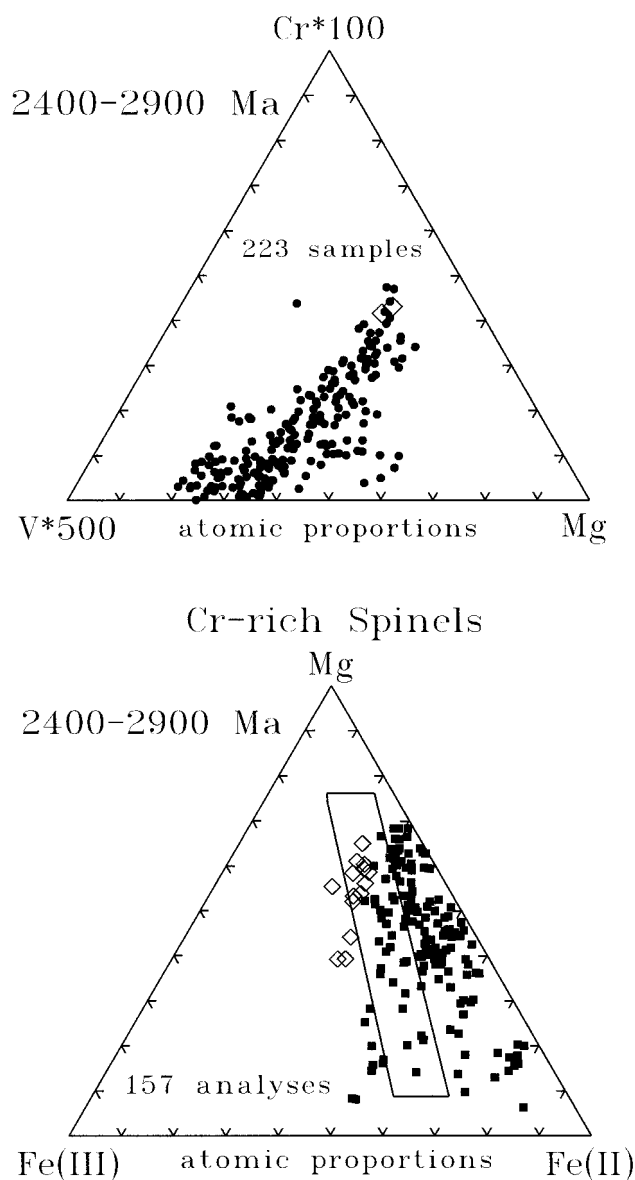


Figure 5c–d. (c) Ternary diagram showing the relative, whole-rock abundances of Mg, Cr, and V in 214 samples of 2400–2900 Ma volcanics. These 223 samples are among the 296 samples that plot within the dashed field of Figure 5a, and where V abundances (in addition to Mg and Cr abundances) were reported (i.e., 73 out of the 296 samples were not analyzed for V abundances). (d) Atomic proportions of Mg, Fe(II), and Fe(III) in 157 Cr-rich spinels from 2400–2900 Ma volcanics. The field of modern Cr-rich spinels from MORB and Hawaiian volcanics (refer to Figure 3a) is shown. Cr-rich spinels from fresh, glass-bearing komatiitic basalts from Belingwe are the open diamonds (Zhou and Kerrich, 1992). Data are from Arndt (1977), Arndt *et al.* (1977), Barnes (1998), Barnes and Hoatson (1994), Cattell and Arndt (1987), Nisbet *et al.* (1987), Roeder and Campbell (1985), and Wilson (1982).

Zimbabwe (Nisbet *et al.*, 1987). The high proportion (88%) of whole-rock samples that satisfy this selection-criterion is supported by previous workers who have independently concluded that many of the whole-rock compositions from the Abitibi Greenstone Belt of Ontario, Canada (Arndt and Nesbitt, 1982; Arth *et al.*, 1977) and Zimbabwe (e.g., Nisbet *et al.*, 1987) have undergone only minor open-system alteration on the whole-rock scale.

Figure 5b contains the 296 whole-rock analyses that plotted within the field shown in Figure 5a. Most of these samples are observed to plot near the FMQ curve that was experimentally defined in Figure 1b. The fresh, glass-bearing komatiitic basalts from Belingwe (open diamonds: Nisbet *et al.*, 1987) also plot near the FMQ curve. The one sample plotting near the IW curve is HB95-24 of Polat *et al.* (1999) from the Superior Province of Canada.

Figure 5c shows the 223 samples out of the 296 whole-rock analyses where V abundances were reported (i.e., 73 of the 296 samples were not analyzed for V). These samples define geochemical behaviors of Cr and V that are similar to that of oxidized modern volcanics (Figure 2c), and clearly distinct from that of reduced lunar samples (Figure 2c).

Figure 5d displays the 157 published analyses of Cr-rich spinels from 2400–2900 Ma volcanics. In comparison to the field of modern Cr-rich spinels defined from Figure 3a, most of these ancient spinels plot outside, and toward the reducing side, of this field. In contrast, the Cr-rich spinels from the fresh, glass-rich komatiitic lavas (Zhou and Kerrich, 1992) from the SASKMAR drill core near Belingwe, Zimbabwe plot within, and on the oxidizing side of, this field.

3.2. 2900–3600 Ma

Published analyses (normalized to 100% on a volatile-free basis) of volcanic samples in the 2900–3600 Ma age-interval have been used in this study from West Greenland (Ameralik Dykes: Gill and Bridgwater, 1979), South Africa (Barberton: Condie *et al.*, 1977; Nesbitt *et al.*, 1979; Nondweni: Wilson *et al.*, 1989), the Superior Province in Canada (Hollings and Kerrich, 1999; Tomlinson *et al.*, 1998), the Aldan Shield in Siberia (Jahn *et al.*, 1998; Puchtel *et al.*, 1993), and the Ukrainian Shield (Samsonov *et al.*, 1996). This geographically diverse set of 140 whole-rock samples are plotted on a volatile-free basis in Figure 6a relative to the field defined in Figure 4 by fresh MORB glasses and Hawaiian volcanics. Forty (40) of the 140 samples that plot outside this field are interpreted as having been chemically altered on the whole-rock scale, and were not used in subsequent figures. The 100 samples from the total of 140 samples (71%) that plot within the field (Figure 6a) are interpreted as having retained their original compositions, and are plotted in Figures 6b and 6c.

Figure 6b contains the 100 whole-rock analyses that plotted within the field shown in Figure 6a. Most of these samples are observed to plot near, or on the oxidized side of, the FMQ curve that was experimentally defined in Figure 1b.

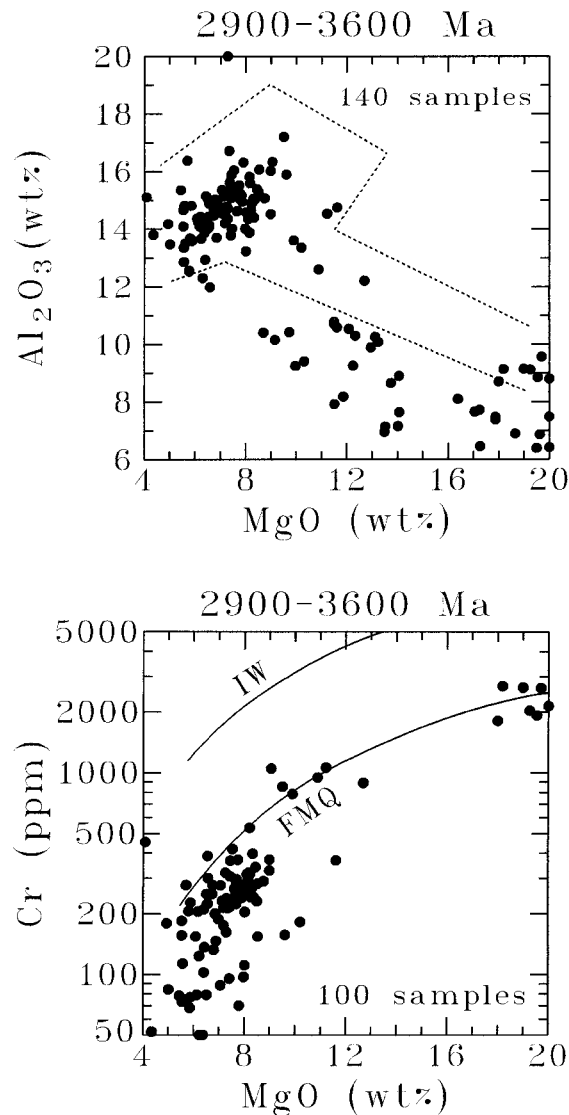


Figure 6a–b. (a) Whole-rock abundances (on a volatile-free basis) of MgO (wt%) and Al_2O_3 (wt%) in 140 volcanics having eruption ages of 2900–3600 Ma. The field defined by the dashed line is from Figure 4 showing the range of compositions among unaltered volcanics. Samples of 2900–3600 Ma volcanics that plot *outside this field* (40 samples) are interpreted as having been chemically altered after their formation and are not used in subsequent figures. 71% of the 140 samples that plot *within this field* (100 samples) are interpreted as having potentially retained their original compositions, and are used in Figures 6b and 6c. Data are from Condie *et al.* (1977), Gill and Bridgwater (1979), Hollings and Kerrich (1999), Jahn *et al.* (1998), Nesbitt *et al.* (1979), Puchtel *et al.* (1993), Samsonov *et al.* (1996), Tomlinson *et al.* (1998), and Wilson *et al.* (1989). (b) Whole-rock abundances (on a volatile-free basis) of MgO (wt%) and Cr (ppm) in the 100 samples of 2900–3600 Ma volcanics that plotted *within the field* shown in Figure 6a. Nearly all of these samples plot near the FMQ line defined in Figure 1b. Data from references listed in Figure 6a.

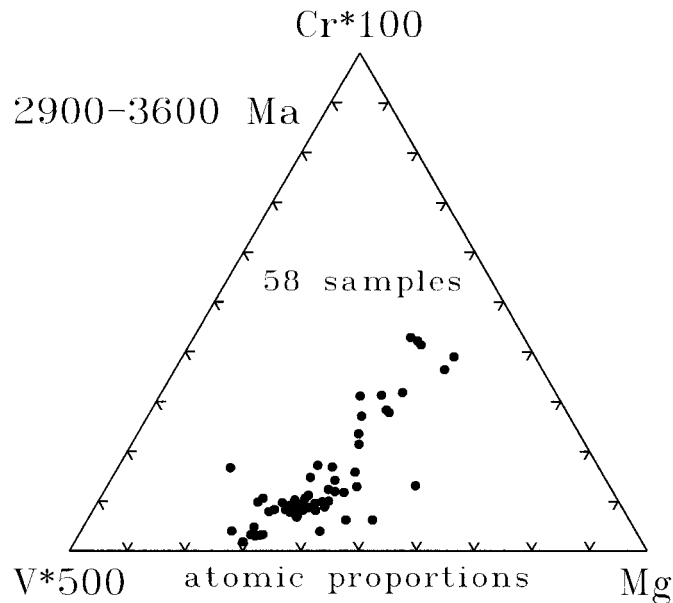


Figure 6c. (c) Ternary diagram showing the relative, whole-rock abundances of Mg, Cr, and V in 58 samples of 2900–3600 Ma volcanics. These 58 samples are among the 100 samples that plot within the dashed field of Figure 6a, and where V abundances (in addition to Mg and Cr abundances) were reported (i.e., 42 out of the 100 samples were not analyzed for V abundances). Data are from Hollings and Kerrich (1999), Jahn *et al.* (1998), Nesbitt *et al.* (1979), Puchtel *et al.* (1993), Samsonov *et al.* (1996), and Tomlinson *et al.* (1998).

Figure 6c shows the 58 samples out of the 100 whole-rock analyses where V abundances were reported (i.e., 42 of the 100 samples were not analyzed for V). These samples define a trend indicating that the geochemical behaviors for Cr and V at the time of their eruption were similar to that of oxidized modern volcanics (Figure 2c), and clearly distinct from that of reduced lunar samples (Figure 2c).

No published analyses for Cr-spinels within igneous rocks in the 2900–3600 Ma have been located by the author at the time of writing of this article.

3.3. 3600–3900 Ma

Compared to samples from the two other age-intervals (i.e., 2400–2900 Ma; 2900–3600 Ma), samples with ages >3600 Ma are: (i) often highly deformed, high-grade metamorphic rocks, such as gneissic terranes; (ii) small in number; and (iii) geographically restricted. These characteristics make interpretation of available geochemical information from these complex rocks intrinsically more difficult.

Figure 7a shows that 36 published whole-rock analyses (normalized to 100% on a volatile-free basis) from northern Labrador (Bridgwater and Collerson, 1976; Nutman *et al.*, 1989), West Greenland (McGregor and Mason, 1977; Nutman and Bridgwater, 1986; Nutman *et al.*, 1984, 1996), and northwestern Canada (Bowring

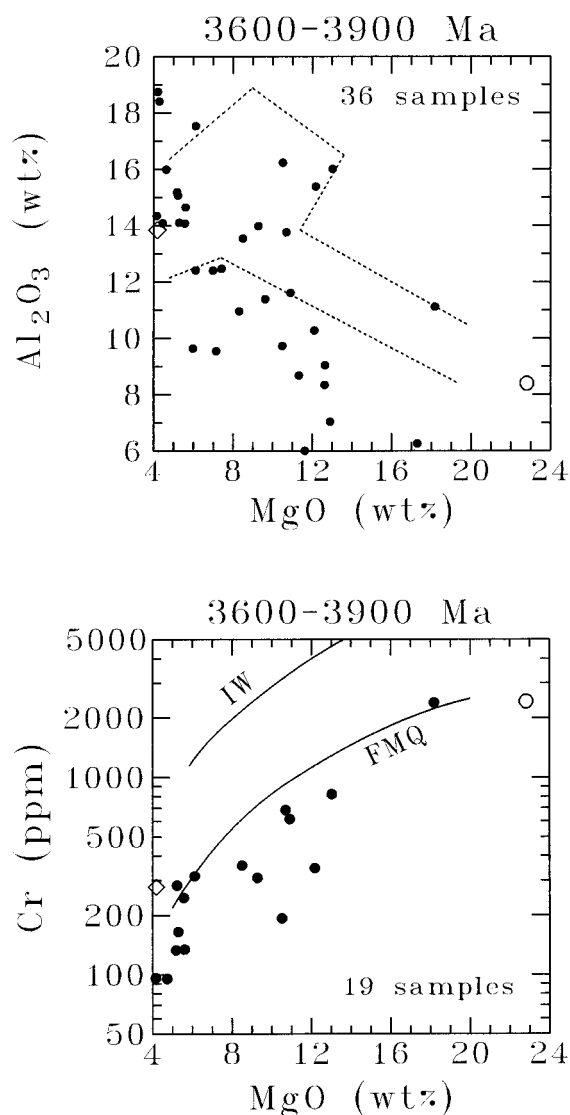


Figure 7a–b. (a) Whole-rock abundances (on a volatile-free basis) of MgO (wt%) and Al_2O_3 (wt%) in 36 samples having ages of 3600–3900 Ma. The field defined by the dashed line is from Figure 4 showing the range of compositions among unaltered volcanics. Samples that plot *outside this field* (17 samples) are interpreted as having been chemically altered after their formation and are not used in subsequent figures. 53% of the 36 samples that plot *within this field* (19 samples) are interpreted as having potentially retained their original compositions, and are used in Figure 7b. The open diamond is 3960 Ma sample (BGXM) from the Acasta region (Bowring *et al.*, 1990). The open circle is a ≥ 3850 Ma metakomatiite from Akilia (S. J. Mojzsis, pers. comm.). Data are from Nutman and Bridgwater (1986), Nutman *et al.* (1984, 1989, 1996), and McGregor and Mason (1977). (b) Whole-rock abundances (on a volatile-free basis) of MgO (wt%) and Cr (ppm) in the 19 samples of 3600–3900 Ma age that plotted *within the field* shown in Figure 7a. Nearly all of these samples plot near the FMQ line defined in Figure 1b.

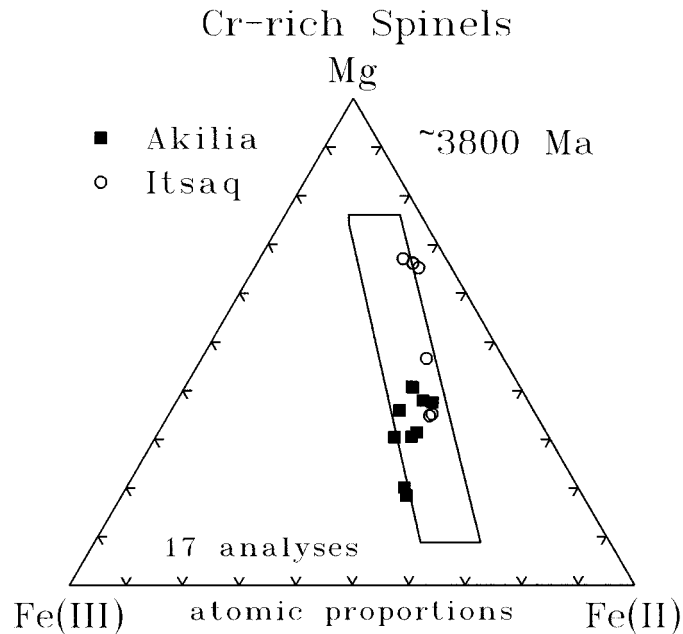


Figure 7c. (c) Atomic proportions of Mg, Fe(II), and Fe(III) in 17 Cr-rich spinels from ~3800 Ma samples. The field of modern Cr-rich spinels from MORB and Hawaiian volcanics (refer to Figures 3a and 3b) is shown. Data are from Chadwick and Crewe (1986: Akilia) and Nutman *et al.* (1996: Itsaq).

et al., 1990). All of the rocks plotted in Figure 7a are interpreted as having formed originally by igneous processes.

Two samples warrant special mention. The first is shown by the open diamond (\diamond) in Figure 7a at $\text{MgO} \approx 4$ wt%. This is a 'layered amphibolitic to tonalitic orthogneiss' (sample BGXM: Bowring *et al.*, 1990) from the Acasta Gneisses in northwestern Canada. This sample has a U-Pb zircon age of 3960 Ma, which has been interpreted as the time of its igneous crystallization (Bowring *et al.*, 1990; Bowring and Williams, 1999). The second sample of special mention is marked by the open circle (O) at $\text{MgO} \approx 23$ wt%. This sample is a metakomatiite (sample SJM/GR/97/3 kindly provided by S. J. Mojzsis) with an age of ≥ 3850 Ma (S. J. Mojzsis, pers. com.) from Akilia Island off the coast of West Greenland. Although this sample has an $\text{MgO} > 20$ wt%, which has been the maximum abundance considered in previous discussions in this article, the scarcity, and thereby importance, of samples of this age is thought to justify its inclusion in the data-base. Since this sample lies within an extension of the dashed field defined originally in Figure 4, this metakomatiite from Akilia is included among the 19 samples (53% of 36 samples) plotted in Figure 7b.

Figure 7b shows the MgO (wt%) and Cr (ppm) abundances in those 19 whole-rock samples that satisfied the selection-criterion in Figure 7a. All of these samples plot near the FMQ curve that was experimentally defined in Figure 1b.

Since none of the 19 samples that satisfied the selection-criterion in Figure 7a have had V abundances reported, a Mg-Cr*100-V*500 ternary diagram is not possible for these rocks.

Analyses of 17 Cr-rich spinels have been reported from Akilia (Chadwick and Crewe, 1986) and Itsaq (Nutman *et al.*, 1996) regions of West Greenland. These Cr-rich spinels (Figure 7c) are similar to Cr-rich spinels in modern volcanics (Figure 3a).

4. Discussion

Whole-rock and Cr-spinel compositions of mafic volcanics from three age-intervals (i.e., 2400–2900 Ma; 2900–3600 Ma; 3600–3960 Ma) suggest that their original oxidation states were near the FMQ buffer at the time of their eruptions. While the oxidation states indicated in Figures 2a, b are at-or-above the FMQ buffer, other methods for estimating the redox states of modern magmas (e.g., Ballhaus *et al.*, 1990; Christie *et al.*, 1986; Gerlach, 1980) arrive at redox states at-or-below the FMQ buffer. One possible explanation is that the Cr, Mg calibration (Figure 1b), which is based on experiments performed at 1-bar total pressure, is not accurately applicable to natural volcanic samples that formed by partial melting of the Earth's mantle at pressures up to 30 kilobars. Since higher pressures would shift the spinel-saturation curves to higher MgO values on Figure 1b, this may account for the offset of the natural samples (Figures 2a, 2b, 5b, 6b, and 7b) from the 1-bar, FMQ curve. Future experiments need to assess the effect of pressure on the locations of the IW and FMQ curves on Figures 2a, b, and related diagrams to assess this matter of redox accuracy. Nonetheless, *with respect to redox precision, a comparison of Figures 2a, b with Figures 5b, 6b, 7b shows no detectable difference (± 0.5 log-unit fO_2) between the redox state of modern volcanic rocks and the original redox state of ancient volcanic rocks.*

The range of Cr-spinel compositions from the 2400–2900 Ma Cr-spinels (solid symbols in Figure 5d) suggests that some of those spinels formed under reducing conditions. This is contrary to results for the whole-rock compositions (Figures 5b, c). The cause of that compositional scatter within a portion of the 2400–2900 Ma Cr-spinels is unknown. The Cr-spinels from the glass-bearing, 2700 Ma komatiitic lavas in the SASKMAR drill core near Belingwe (open diamonds in Figure 5d), which would seem to be the best candidates for having retained their original redox memory (Nisbet *et al.*, 1987), indicate an initial oxidation state near the FMQ buffer, in agreement with the whole-rock data (Figures 5b, c).

With the exception of the compositional scatter among a portion of the 2400–2900 Ma spinels (Figure 5d), the Earth's mantle appears to have been at-or-near its

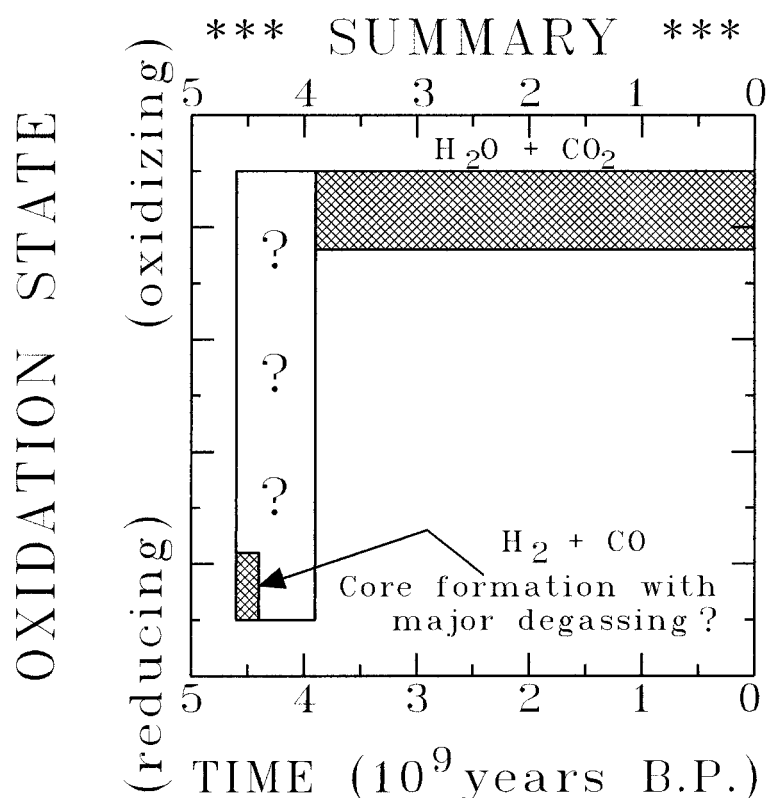


Figure 8. Cartoon summarizing the redox history of mafic volcanics, and hence of the Earth's upper mantle during the last >3850 Ma. Gases released by high-temperature volcanism would have been dominated by H₂O and CO₂ during this interval. The composition of volcanic gases prior to that time remains unknown. Nonetheless, the Earth's mantle appears to have achieved its current oxidation state (~FMQ) by at least 3600 Ma, and possibly by at least 3960 Ma.

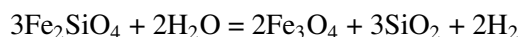
current oxidation state since at least 3600 Ma (Figures 6b, c), and probably since at least ~3900 Ma (Figures 7b, c). These should be regarded as being minimum ages for when the Earth's mantle achieved its current oxidation state (Figure 8). Whenever that occurred, gases emitted by high-temperature, mantle-derived magmas have since been dominated by H₂O, CO₂, and SO₂, which is a mixture of gases known to provide relatively small yields of prebiotic molecules (e.g., Miller, 1998; Zolotov and Shock, 2000).

The results from the current investigation are derived from volcanic rock-types that are generally thought to have been the most widespread form of volcanism throughout all, or most, of Earth's history. Consequently, it seems plausible that the gases accompanying these voluminous eruptives would have been a significant component to the Earth's atmosphere. In contrast, some diamond-bearing assemblages from the upper mantle are reported to have more reduced oxidation states (between the IW and FMQ buffers; Daniels and Gurney, 1991; Haggerty and

Toft, 1985). The significance of those isolated regions in the mantle for the nature of volcanic gas compositions through time remains unknown. However, if those more reduced regions are ancient enclaves of a more widespread condition inside the Earth (e.g., Ballhaus *et al.*, 1990; Kasting *et al.*, 1993), then to be consistent with the results presented in the current study, they survive from ≥ 3900 Ma.

The model of Kump *et al.* (2001), which involves an abrupt increase of the mantle's oxidation state to near current levels at ~ 2500 Ma, is not supported by this current study. For example, Figures 6 and 7 show no evidence for those portions of the mantle associated with widespread mafic and ultramafic volcanism having been at a reduced state prior to ~ 2500 Ma.

Apart from having attained its current oxidation state by ≥ 3900 Ma, the exact timing and processes by which the Earth's mantle initially attained its current oxidation state remain unknown. Stevenson (1983) suggested that the mantle may have convected vigorously during the first 200 Ma with turn-over times estimated to be in the range of only 10^4 to 10^6 yr. With such vigorous convection, subduction of oxidized/hydrated surface materials into the



mantle may have resulted in rapid consumption of any residual vestiges of the core-forming alloy in the mantle leading to the current oxidation state of the Earth's interior. The release of H_2 followed by its hydrodynamic loss from the atmosphere during the first 200 Ma when the Sun was highly active in the ultraviolet portion of the spectrum (e.g., Dreibus and Wanke, 1987; Holland, 1962, 1978, 1984; Hunten, 1993; Kasting, 1993; Owen, 1998; Walker, 1990) may have led to an early, irreversible oxidation of the Earth's mantle (perhaps by 4300 Ma). Evidence to test this speculation is currently being gathered.

5. Conclusions

In agreement with earlier views (e.g., Abelson, 1966; Canil, 1997; Chang *et al.*, 1983; Holland, 1962; Rubey, 1955; Walker, 1990), this study indicates that the gases released into the atmosphere by high-temperature volcanic eruptions have been dominated by H_2O , CO_2 , and SO_2 since at least 3600 Ma, and probably since at least ~ 3900 Ma. Mantle-derived volcanic gases that entered the atmosphere from high-temperature volcanism would have provided low, but not zero (e.g., Miller, 1998; Zolotov and Shock, 2000), yields of prebiotic molecules during that interval.

Although the current results indicate that high-temperature volcanism could not have been a significant source of reduced gases to the atmosphere since at least ~ 3900 Ma, it does not necessarily mean that the Earth's atmosphere has not been chemically reducing during some part of the last ~ 3900 Ma. If the atmosphere was

reducing (e.g., CH₄, H₂, H₂S, NH₃, CO) at any time during the last ~3900 Ma, high-temperature volcanic outgassing was not the cause of it.

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