

INHIBITION OF SINTERING BY Si DURING THE CONVERSION OF Si-RICH FERRIHYDRITE TO HEMATITE

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Abstract—The distribution and chemical state of Si in a synthetic 2-line ferrihydrite with a Si/(Si + Fe) molar ratio of 0.11 was studied. Heat treatment under oxidizing conditions shows that Si-rich ferrihydrite is stable to 400°C. The transformation to hematite and the formation of a polymerized amorphous-silica phase occur at 850°C. At this temperature, the specific surface area decreases greatly and the average pore diameter increases, which is indicative of sintering. Heating under severe reducing conditions causes a segregation of Si from Fe and results in a mixture of elemental Fe and SiO₂. Surface and structural data suggest that Si is located near the particle surface where it limits the rearrangement of Fe octahedra to form hematite.

Key Words—BET, Ferrihydrite, Si, Sintering, XPS.

INTRODUCTION

Ferric oxides are among the most intensively studied metal oxides because of their prevalence in natural systems and their importance in technological applications, such as in pigments and catalysts (*e.g.*, Zhao *et al.*, 1994). The high chemical reactivity that is common in these materials is due in part to the high specific surface area. Ferrihydrite, a poorly crystalline ferric oxide with an approximate formula of Fe-OOH·0.4H₂O (*e.g.*, Zhao *et al.*, 1994), has a high surface area, which ranges from 200 to 800 m²/g (*e.g.*, Stanjek and Weidler, 1992). Ferrihydrite is metastable with respect to goethite (α -FeOOH) and hematite (α -Fe₂O₃).

Upon heating, pure ferrihydrite converts to hematite between 300–400°C (*e.g.*, Carlson and Schwertmann, 1981; Stanjek and Weidler, 1992). Furthermore, precipitating ferrihydrite in a solution containing Si is known to increase the thermal stability of ferrihydrite so that transformation to hematite is delayed by several hundred degrees (*e.g.*, Herbillon and Tran Vinh An, 1969; Childs *et al.*, 1993). Several authors attributed the higher thermal stability of Si-rich ferrihydrite to surface effects of Si, *i.e.*, the formation of Si-O-Fe bonds that inhibit the dehydroxylation and the subsequent atomic rearrangement to hematite (Herbillon and Tran Vinh An, 1969; Zhao *et al.*, 1994). Pure and Si-rich ferrihydrites may, however, dehydroxylate without transforming to hematite (Stanjek and Weidler, 1992; Childs *et al.*, 1993). Another possibility is that Si substitution causes increased stability. Based on X-ray photoelectron spectroscopy (XPS) data, Vempati *et al.* (1990) postulated that Si is structure bound in

ferrihydrite. On the other hand, Yoshinaga and Kanasaki (1993) precipitated ferrihydrite in the presence of Si and Ge, which have significantly different ionic radii, and concluded from the similarity in *d*-values that these elements did not substitute in the ferrihydrite structure. Parfitt *et al.* (1992) proposed a model where silicate bridges the surfaces of ferrihydrite domains, which aggregate to form primary particles. The rearrangement of Fe octahedra to form hematite is inhibited by the Si in those particles.

Observing the conversion of ferrihydrite and the associated Si under different conditions may provide a better understanding of the nature of the Si-O-Fe bonds. This study presents new structural and surface-specific data recorded under various chemical conditions, to determine the mechanism by which Si inhibits the conversion of ferrihydrite to hematite.

MATERIALS AND METHODS

The sample was precipitated from 0.25 M Fe(NO₃)₃ in the presence of 0.1 M Si, prepared from Na₂SiO₃, and 2 M NaOH. The initial pH was 12.7. The resulting reddish suspension was aged for 660 d at 20°C and shaken periodically. During aging the pH decreased to 12.5. The aged precipitate was carefully washed by two cycles of centrifugation and resuspension in distilled, deionized water (di), followed by dialysis in di until the conductivity of the dialysis water was equal to that of fresh di (Glasauer, 1995). After dialysis, the pH of the suspension was 8.5. No precautions were taken to exclude CO₂ during synthesis and dialysis. The Si/(Si + Fe) molar ratio was determined by atomic absorption spectroscopy (AAS, Unicam 939) after acid dissolution (20 mg dried oxide in 1 mL 6 M HCl, immediately diluted to 25 mL).

The point of zero charge (pzc) was measured by salt titration with NaNO₃ after the method of Kinniburgh

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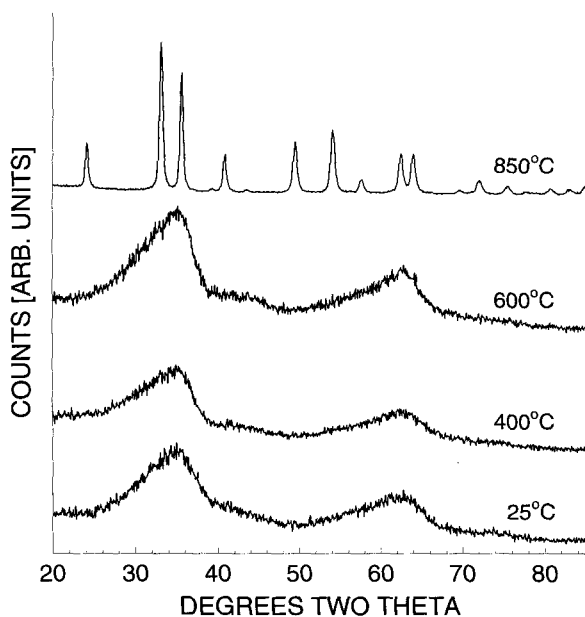


Figure 1. X-ray diffraction pattern of untreated Si-rich ferrihydrite and after heating at 400, 600, and 800°C.

et al. (1995). In brief, an amount of solid suspension to yield ~ 75 m² of surface was diluted to ~ 100 mL with di water. The pH was adjusted to 4 and the suspension outgassed overnight under an N₂ atmosphere to remove adsorbed CO₂. An automatic burette delivered concentrated NaNO₃ solution to give salt concentrations of 0.005, 0.01, and 0.1 M. Suspensions were titrated with NaOH and HNO₃ between pH 4–8.5. The entire procedure required ~ 12 h.

The structure and surface properties of the precipitate at room temperature (RT) and after heating for 1 h at 400, 600, and 850°C were analyzed by XRD (powder X-ray diffractometry; Syntac XDS 2000; CuK α radiation) and by N₂ adsorption (BET method; for details see Gregg and Sing 1982; Micromeritics Gemini 2360 apparatus, static system). For the XRD analyses, scans were made from 20 to 90 $^{\circ}2\theta$ in steps of 0.075 $^{\circ}2\theta$ and 20 s counting time. The BET specific surface area was determined by N₂ adsorption at the temperature of liquid nitrogen, and the pore-size distributions were calculated following the BJH method (Barrett *et al.*, 1951). Prior to the BET measurements, the samples were heated at 90°C in a steady flow of nitrogen for 24 h, as described by Weidler (1997). Fourier transform infrared (FTIR) spectra of the untreated and heat-treated samples were recorded in the mid-infrared range from 400 to 1200 cm⁻¹ on a Nicolet 510 spectrometer in absorbance mode on KBr pellets. The weight loss of the Si-rich ferrihydrite between RT and 1000°C was measured in O₂ by thermogravimetry (TG; TGS-2, Perkin-Elmer).

XPS was performed on thin pressed pellets of freeze-dried samples, using a Kratos 5800 XPS spectrometer operated at a base pressure of 5×10^{-10} torr, with monochromatic MgK α (1253.6 eV) radiation as the energy source. The energy scale was calibrated using gold foil and the Au(4f_{7/2}) peak. The hemispherical analyzer was operated at a constant-pass energy of 40 eV with an energy resolution of 1.0 eV (Ag 3d_{5/2}). Spectra were recorded of the untreated ferrihydrite, after heating at 400°C for 30 min in an O₂ atmosphere, and after heating at 600°C for 15 min in H₂, *i.e.*, under reducing conditions. The latter procedure has a selectively harsher impact on Fe³⁺ than on Si. Ferric iron is expected to undergo chemical changes under these conditions, whereas Si is chemically stable. The software program Kratos ds800 was used to evaluate the data. For the untreated and heated samples, the binding energies for Fe(2p_{3/2}) and O(1s) were considered. To evaluate Si, the Si(2s) signal was mostly considered, rather than the Si(2p) signal, which can superimpose on the Fe(3s) peak (McIntyre and Zetarak, 1977).

RESULTS AND DISCUSSION

After aging for 60 d, the precipitate consisted of a single solid phase (Figure 1) that was identified as a typical 2-line ferrihydrite by XRD (*e.g.*, Stanjek and Weidler, 1992). No chemical conversion of the ferrihydrite was found after aging for 660 d. The Si/(Si + Fe) molar ratio of the precipitate was 0.11, compared to the initial ratio of 0.29. Because the same synthesis procedure without Si in solution results in well-crystallized goethite (Glasauer, 1995), the stability of the 2-line ferrihydrite suggests that Si suppresses the conversion to a more crystalline phase.

The pzc value of 6.4 for this Si-rich ferrihydrite was significantly lower than for pure ferrihydrite, which has a value of ~ 8 (Schwertmann and Fechter, 1982). This indicates that at least part of the coprecipitated Si is located at the surface.

Stepwise heating of Si-rich ferrihydrite followed by XRD revealed that this phase was stable to $<400^{\circ}\text{C}$ (Figure 1). First structural changes were observed after heating at 600°C, as indicated by the decreased full width at half maximum height (FWHM) from 7.8 to 6.3 $^{\circ}2\theta$ and asymmetry of the peak at 35 $^{\circ}2\theta$. The shape of the peak near 36 $^{\circ}2\theta$ suggests that hematite was beginning to form. The complete decomposition of Si-rich ferrihydrite occurred after heating at 850°C and a well-crystallized hematite was formed (Figure 1). Based on Rietveld refinement (17 varied parameters, R-Bragg Parameter, R_B = 3.1%), unit cell parameters of $a = 0.5307 \pm 0.0002$ nm and $c = 1.3748 \pm 0.0003$ nm were determined, and they are similar to pure hematite (ICDD card #33-664). Thermogravimetry exhibited dehydroxylation of the Si-rich ferrihydrite at $\sim 550^{\circ}\text{C}$ with a relative weight loss of 20.6%. Comparison with XRD data suggests that Si

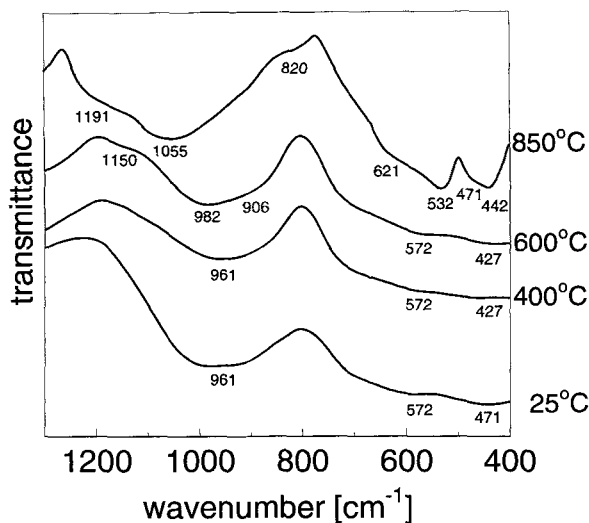


Figure 2. Mid-infrared spectra of untreated Si-rich ferrihydrite and after heating at 400, 600, and 800°C.

stabilizes dehydroxylated ferrihydrite as previously reported (e.g., Herbillon and Tran Vinh An, 1969).

The FTIR analysis of the untreated sample yielded broad bands at ~ 471 and ~ 572 cm^{-1} , characteristic of ferrihydrite, and at ~ 961 cm^{-1} , typical for Si-O vibrations (Farmer, 1974; Moenke, 1974). Only small changes were observed after heating at 400 and 600°C (Figure 2). After heating at 850°C, new features characteristic for lattice vibrations of hematite at 442, 532,

and 621 cm^{-1} occurred (Farmer, 1974). Furthermore, the broad Si-O peak was shifted to 1055 cm^{-1} , and pronounced shoulders at 1191, 820, and 471 cm^{-1} occurred. These bands are characteristic of amorphous SiO_2 , most likely a dehydroxylated polymerized phase (Moenke, 1974; Schwertmann and Thalmann, 1976).

The BET analysis showed an effect of heating on the specific surface area and pore-size distribution (Figure 3). According to International Union for Pure and Applied Chemistry (IUPAC) classification (Sing *et al.*, 1985), the N_2 -adsorption isotherm for the untreated sample could be assigned to Type I, whereas the isotherm for the sample heated at 850°C is Type II (Figure 3a). The isotherms of the samples heated at 400 and 600°C exhibited a combination of the two types. Type I isotherms (Langmuir-type isotherms) are found for microporous material or powders, whereas Type II isotherms are characteristic for non-microporous materials.

The untreated sample was microporous and mesoporous, and had a specific surface area of 399 m^2/g . Upon heating at 400 and 600°C, the specific surface area decreased to 222 and 183 m^2/g , respectively. The mean pore diameter increased simultaneously from 2.3 nm at RT to 3.2 nm at 600°C. Further heating at 850°C caused a reduction of the BET area to 37 m^2/g . No significant microporosity was detected, and the average pore diameter increased to 10.2 nm. The pore-size distribution curves indicate that heating at 850°C drastically reduced the number of micropores (< 2 nm)

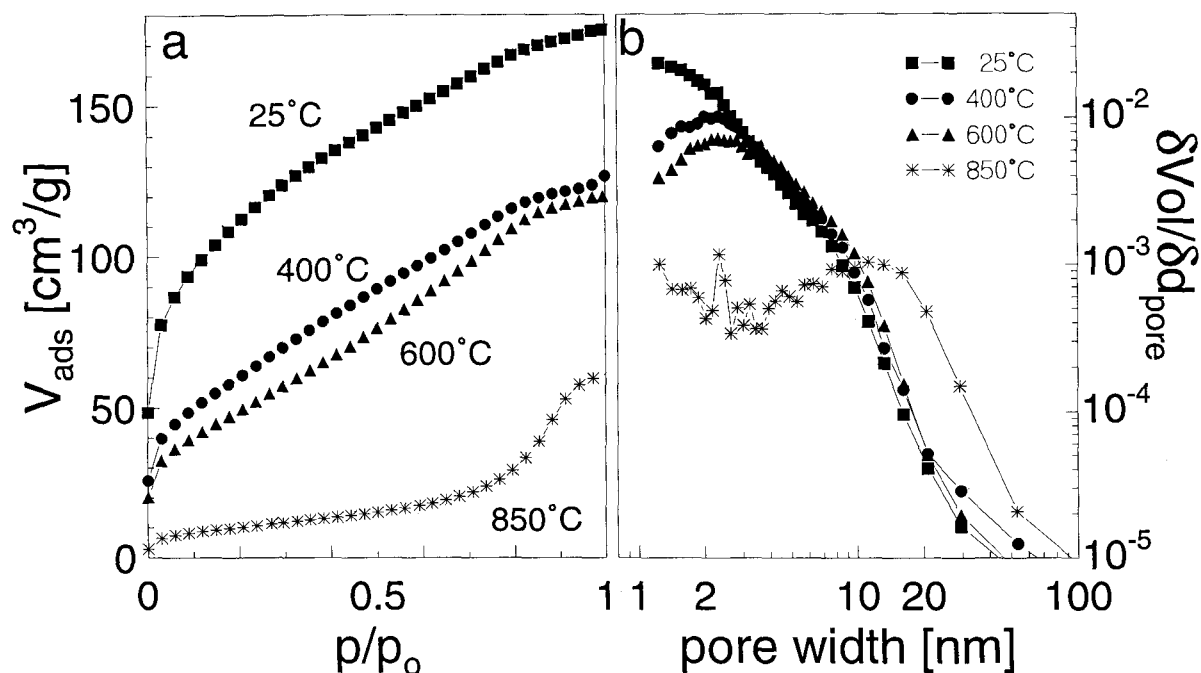
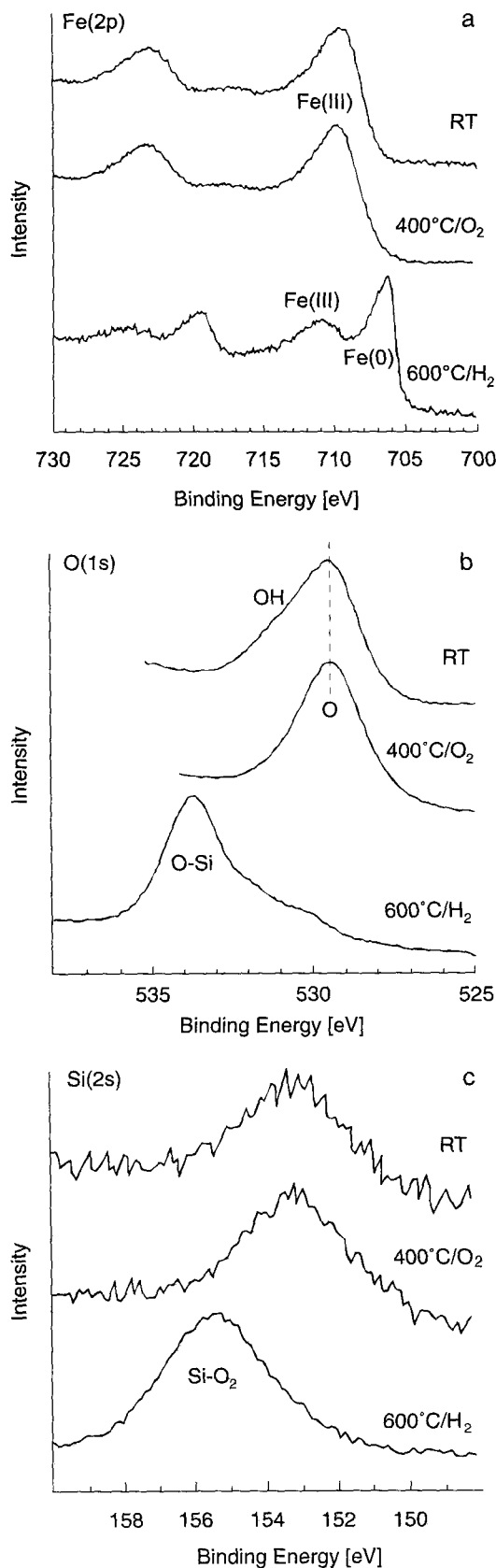


Figure 3. The N_2 isotherms (a) and pore-size distribution curves (b) of untreated Si-rich ferrihydrite and after heating at 400, 600, and 800°C.



(Figure 3b). The fraction of mesopores (2–50 nm) of size >4 nm did not change significantly until the sample was heated at 850°C. After this treatment, the sample exhibited a wider pore-size distribution and a shift to larger pore diameters. The fraction of pores at the micropore/mesopore range (2 nm) after heating at 850°C was about two orders of magnitude lower than the micropore fraction of the untreated sample. The reduction in the specific surface area and the increased pore-size diameter after heating is indicative of sintering.

The XPS data showed the effects of thermal treatment on Fe- and Si-bonding environments. Because electron escape depths in the XPS analysis are ~1–5 nm (Hochella, 1988), and the mean diameter of the ferrihydrite particle is ~4 nm, the XPS results provide information on surface and on bulk properties of primary ferrihydrite particles, as well as of aggregates. In the untreated sample, a band for Fe(2p_{3/2}) occurred at 711–710 eV, indicating trivalent Fe (McIntyre and Zetaruk, 1977) (Figure 4a). For O(1s), an asymmetric peak in the range 535–527 eV, with a maximum at 530 eV, was found (Figure 4b). Use of an 80% Gaussian/20% Lorentzian mixed function resolved this band into two peaks, at 530 and 531 eV. The peak at 530 eV was assigned to O(1s) bound in ferric oxides (McIntyre and Zetaruk, 1977). The shoulder at higher energy was attributed to O(1s) coordinated in hydroxyl groups associated with Fe (Vempati *et al.*, 1990). The Si(2s) peak occurred at 153.3 eV (Figure 4c). The Si(2p) signal is commonly used in XPS analysis because of its high intensity; however, the broad satellite peak of the Fe(3s) signal at ~104 eV (McIntyre and Zetaruk, 1977) can interfere with the Si(2p) signal. Since the Si(2s) binding energy of quartz is 154.4 eV (Seyama and Soma, 1985), the lower value we determined indicates the absence of a three-dimensional SiO₂ phase. This value is also significantly lower than the value of 154.1 eV determined by Soma *et al.* (1996) for a synthetic 7-line ferrihydrite, which is probably a result of the higher final Si content of their sample and differences in the preparation method. The data do, however, provide evidence for an Si-O-Fe bond, and agree well with the observation that bonds with transition metals cause a shift to lower binding energies owing to an increase of the electron density on Si (Paterson and Swaffield, 1994). The symmetry of the Si peak suggests that the Si associated with the ferrihydrite occurs in a similar bonding environment. Upon heating the sample at 400°C in an O₂ atmosphere, no changes for the Fe and Si signals were

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Figure 4. XPS spectra from (a) 730–700 eV showing peaks for Fe(2p_{3/2}), (b) 538–525 eV for O(1s), and (c) 159–151 eV for Si(2s) at RT, at 400°C in O₂, and at 600°C in H₂.

found (Figure 4a and 4c). The O(1s) peak became more symmetric, but the position of the maximum was identical to those at lower temperature (Figure 4b). Based on the thermogravimetric data, this change is explained as initial dehydroxylation in the Si-rich ferrihydrite.

By contrast, drastic changes in the Fe(2p_{3/2}), O(1s), and Si(2s) electron binding energies occur after heating the sample at 600°C in an H₂ atmosphere. Under these reducing conditions, a strong band at 707 eV occurs and the peak at 711–710 eV decreases in intensity (Figure 4a). The dominant sharp peak at 707 eV is characteristic of elemental Fe (McIntyre and Zetaruk, 1977). The traces of the Fe³⁺ signal persisted, however, and showed that the reduction of Fe was not complete. The O(1s) peak shifted to higher binding energies after treatment under reducing conditions, and exhibited a maximum at 533.8 eV (Figure 4b). This peak is characteristic of the O(1s) binding energy in SiO₂ (Perkin-Elmer, 1979). The shift of the Si(2s) peak to a higher binding energy of 155.3 eV also indicates the formation of a SiO₂ phase (Figure 4c).

The XPS data provide evidence for Si-O-Fe bonds, but no local structural assignment of these bonds can be made. Note that the terms “bulk” and “surface” differ significantly for small ferrihydrite particles. Assuming an average diameter of a ferrihydrite particle of 3.8 nm (based on a surface area of 400 m²/g from BET analysis and assuming spherical particles), and considering that the first two to three oxygen-atom planes influence the surface properties, a range in the ratio of surface area to bulk volume is calculated at ~2:1 to 9:1. Hence the particle is primarily composed of surface area and near-surface area, and this suggests that the bulk structure is of lesser significance. Vempati *et al.* (1990) argued that >90% of associated Si is structure bound in a ferrihydrite precipitated at a Si/Fe molar ratio of 1.0 (see Vempati *et al.*, 1990, Figure 3). This conclusion is based on the XPS Si(2p) signal, which occurs in an energy range where Fe(3s) has a satellite peak.

Si changes the pzc of ferrihydrite substantially, and thermal conversion produces two separate phases with no evidence for substitution. These results suggest that Si is associated with ferrihydrite surfaces, which is consistent with XPS results of Soma *et al.* (1996). They indicate that Si is mainly present as silicate bridging the surfaces of crystalline domains within primary particles, and bridging primary particles within aggregates.

Parfitt *et al.* (1992) suggested a model where the linking of ferrihydrite domains by Si suppresses the rearrangement of Fe octahedra to form hematite. In this model, the Fe-O-Si bonds must be broken before the conversion of Si-rich ferrihydrite to hematite or other Fe phases occurs. The spectroscopic and BET results are in good agreement with this model, because

the growth of particles occurs in the same temperature range where the breakage of the Fe-O-Si bonds and the growth of hematite occur. Hence, the increase in the conversion temperature of ferrihydrite associated with Si is mainly the result of an inhibition of sintering by Si.

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