Boron Release from Weathering of Illites, Serpentine, Shales, and Illitic/Palygorskitic Soils

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ABSTRACT

Despite extensive research on B adsorption and release from soils, mineral sources of B within natively high B soils remain poorly understood. The objectives of this study were to identify source minerals contributing to the continued B release after extraction of soluble B and to estimate B release rate from weathering of B-containing minerals and soils. Two specimen illites (Morris and Fithian), two shales (Salt Creek and Moreno Gulch), a fresh and a weathered serpentine (antigorite) from the Coastal Range of California, a Traver silt loam (coarse-loamy, mixed, superactive thermic Natric Haploxeralfs) and a Twisselman clay loam [fine, mixed (calcareous), superactive thermic Typic Torriorthents] both containing illite and palygorskite were successively extracted 7 to 26 times following each 12-h equilibration in 0.1 and 0.01 *M* $CaCl_2$ solution until the supernatant solutions contained less than the detection limit of 0.001 mmol B L^{-1}. Subsequently, the $<$2-μm and 2- to 20-μm size fractions were separated and reacted in deionized water at pH 5, 7, and 9 adjusted with HCl and NaOH. The total B of the separated fractions ranged from 5.1 to 28 mmol B kg^{-1} and the surface areas from 5.7 to 126 m^2 g^{-1}. Boron release rates decreased with time and increasing pH. Average B release rates from 150 to 180 d ranged from 0.005 fmol m^{-2} s^{-1} for Salt Creek shale (2–20 μm) to 0.342 fmol m^{-2} s^{-1} for Traver silt ($<$2 μm) at pH 5, 0.004 fmol m^{-2} s^{-1} for Salt Creek shale (2–20 μm) to 0.060 fmol m^{-2} s^{-1} for Traver silt ($<$2 μm) at pH 7, and 0.002 fmol m^{-2} s^{-1} for weathered serpentine (2–20 μm) to 0.044 fmol m^{-2} s^{-1} for Traver silt ($<$2 μm) at pH 9. Nonstoichiometric dissolution was found for all materials at all pH levels. Illite, chlorite, and palygorskite were identified in the clay and silt fractions of the soils. Boron release from the two soils was accompanied with high Mg release into the solution, suggesting palygorskite as a major source for B.

Boron is an element of great concern because for many plants the ratio of toxic to adequate B concentrations is the smallest among the essential micronutrients. Boron concentrations in soil water in the range of 0.05 to 0.5 mmol L^{-1} have a deleterious effect on plant growth (U.S. Salinity Laboratory Staff, 1954; Gupta et al., 1985). Toxic levels of B have been frequently reported in the soils and irrigation waters of many arid and semiarid regions of the world, including the irrigated areas of the western USA (Rhoades et al., 1970; Keren and Bingham, 1985). Boron toxicity was reported to overshadow other salt effects for several crops in a study of the long-term effects of using saline water for irrigation (Hanks et al., 1986).

Soil salinity and B toxicity have been repeatedly studied in the central and south part of the western San Joaquin Valley of California. Alluvial deposits in the valley derive primarily from Coast Ranges of California, which are composed of several nearly parallel ranges of north-northwest trending mountains and intervening valleys (Presser et al., 1990). The Coast Ranges evolved as a result of complex folding and faulting of geosynclinal sedimentary rocks of Mesozoic and Tertiary age. The geomorphic character of the alluvium laid down by streams draining the east-central Coast Ranges reflects late Cenozoic uplift of the foothills and subsidence of the valley (Lettis, 1982). The semiarid climate and the geological settings of the valley have contributed to soil salinization and toxic levels of B.

The presence of excess soluble B in arid lands is usually attributed to the weathering of B-containing soil minerals or the utilization of high B irrigation waters (U.S. Salinity Laboratory Staff, 1954). Rhoades et al. (1970) observed increased B concentrations in soil column effluents following a period of postreclamation storage and termed the phenomenon "boron regeneration," which is attributed to the continued release of sparingly soluble sources of B. Boron regeneration was also reported in a high B soil reclaimed in the field (Bingham et al., 1972). Postreclamation desorption of B and redistribution of B by diffusion from bypassed to leachable soil pore regions are additional mechanisms for regeneration (Peryea et al., 1985a, 1985b, 1985c).

Boron is adsorbed by soil solids, and distributed between soil water and solid phases. A detailed review on the characteristics of B adsorption on different soil constituents is given by Goldberg (1993). Boron activity in the soil solution is unlikely to be controlled by a solid phase mineral. Tourmaline is often the only B mineral found in soils but it is extremely resistant to weathering; whereas, hydrated B minerals form as evaporite deposits from saline lakes and are too soluble to persist in most soils (Goldberg, 1993). The readily soluble and specifically adsorbed (inner-sphere complexed) B fractions was reported to account for on average $<$2% of the total B in 24 surface soils from Ontario, Canada (Hou et al., 1994). Recent infrared spectroscopic evidence supports the formation of inner-sphere complexation of B with mineral surface functional groups (Su and Suarez, 1995). They postulated that adsorbed B might be responsible for controlling B activity in the soil solution.

Boron desorption has received less attention than B adsorption, yet it is as important to B availability in soils. Many soils exhibit hysteresis in adsorption-desorption process. Desorption did not follow the adsorption iso-

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Abbreviations: CEC, cation-exchange capacity; DI, deionized water; ICP-AES, inductively coupled plasma-atomic emission spectrometry; XRD, X-ray diffraction.

therm in Hawaiian kaolinitic soils (Okazaki and Chao, 1968) and in soils from California, Utah, and Idaho that presumably contain illites and smectites (Rhoades et al., 1970). Boron desorption from 6 out of 10 New Mexico soils containing montmorillonite, mica, and kaolinite could not be fit with the same Freundlich parameters for B adsorption (Elrashidi and O'Connor, 1982). The tendency for desorption to be slower than adsorption was not correlated to any soil property measured, nor was it explainable in terms of existing literature (Elrashidi and O'Connor, 1982).

Boron desorption kinetics have been described by various equations, including the first-order rate equation (Griffin and Burau, 1974; Sharma et al., 1989), the Elovich reaction rate equation (Peryea et al., 1985b; Sharma et al., 1989), and the power function (Sharma et al., 1989). A limitation of these rate equations is that their general applicability to numerous unrelated reaction processes implies that they may be primarily a mathematical fitting of kinetic data. For example, the Elovichian behavior of sorbing or desorbing constituents in soil systems may be fortuitous (Smith et al., 1971). Rate equations alone cannot provide accurate information on the mineral sources of B released from soil. To predict B release from soils, we need information on B release from individual minerals and effects of surface area and chemical variables such as pH on these minerals.

Illite is often a dominant clay mineral in California soils, and illites contain higher native B than other phyllosilicate clays do. Serpentine and marine shales are widespread in the west Coast Ranges of California. There is abundant evidence that serpentine weathers initially to smectite (eg., Wildman et al., 1968, 1971). A study of the B release characteristics of the representative materials including illites, shales, and serpentine is necessary to our understanding of B behavior in California Central Valley soils. Knowledge of long-term B leaching from high B containing irrigated soils is essential for prediction of future B contamination in drainage waters.

Our objectives in this study were to: (i) obtain information on B release rates after the readily leachable B is removed from specimen illites, soil parent materials, and soils so that the long-term release of B from these materials can be evaluated; (ii) identify mineral sources of slowly released B in representative soils from the west side of the San Joaquin Valley.

MATERIALS AND METHODS

Two specimen illites (Morris and Fithian) were obtained from Ward's Natural Science Establishment, Inc. (Rochester, NY). We collected weathered serpentine and fresh serpentine rock (Jurassic to lower Miocene marine origin, Big Blue Formation), Salt Creek shale (Eocene to Oligocene, marine sediments, Kreyenhagen Formation), and Moreno Gulch shale (Late Cretaceous to Paleocene, marine sediments, Moreno Formation), all from the west Coast Ranges of California (Presser et al., 1990). Both serpentine materials had a pH of 9.2 in water (w/v, 1:2); whereas, both shales were acidic, with a pH of 4.0 (w/v, 1:2). Two surface horizon (0–20 cm) soil samples (Traver silt loam and Twisselman clay loam) were collected from minimally disturbed sites adjacent to irrigated cropland in southern San Joaquin Valley. These sites were near the sites described by Peryea et al. (1985a, 1985b, 1985c). Both soils are saline and sodic. The Traver silt loam is classified as coarse-loamy, mixed, superactive thermic Natric Haploxeralfs. The Twisselman clay loam is a fine, mixed (calcareous), superactive thermic Typic Torriorthents. The specimen illites and serpentine materials were air dried, crushed in an electrical mill, and passed through a 50-μm sieve, while the shales and soil samples were air dried, hand ground with mortar and pestle, and passed through a 250-μm sieve.

A multiple batch extraction technique was used to eliminate the effects of solute bypass and intra-aggregate diffusion, which make B release from column experiments difficult to interpret. All samples were extracted with consecutive, 12-h, 1:10 solid/aqueous solution reaction (0.1 *M* $CaCl_2$ for the first three extractions and 0.01 *M* $CaCl_2$ for the continuing extractions). The air-dry equivalent of 25.0 g of oven-dry material per bottle was placed into acid-washed 250-mL polypropylene centrifuge bottles (12 to 24 bottles per material). Sufficient $CaCl_2$ solution was added to bring the total solution volume to 250 mL. The suspensions were shaken on a reciprocating shaker for 12 h and centrifuged. The supernatant was removed and replaced with fresh extractant. Boron in duplicate supernatant was passed through 0.1-μm Whatman filters (Whatman Ltd, Maidstone, UK) and determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The extraction continued until the B concentration in the supernatant was below the detection limit of 0.001 mmol L^{-1}.

The extracted materials were saturated with Na^+ by repeatedly washing with 1.0 *M* NaCl before particle-size separation in deionized (DI) water. The clay (<2 μm) and fine-silt (2–20 μm) size fractions were separated from the samples by sedimentation, and then saturated with Ca^{2+} by washing with 0.5 *M* $CaCl_2$. Excess $CaCl_2$ was removed by washing the fractions repeatedly with DI water. The clay and fine-silt fractions were air-dried and gently ground with mortar and pestle.

Total elemental analysis of the separated fractions was performed by Na_2O_2 fusion in conjunction with ICP-AES (Potts, 1987) with some modifications. For determination of metallic elements, B, and S, air-dry equivalent of 0.250 g of oven-dry sample was fused with 1.0 g of Na_2O_2 at 700°C in a zirconium crucible for 2 h (the melting point of Na_2O_2 is 480°C). The cooled melt was extracted into cold water in the crucible and any insoluble hydroxides were dissolved by adding 5 *M* HCl. The contents in the crucible were transferred to a 250-mL volumetric flask, excess HCl being added to a final concentration of 0.4 *M* HCl in a 250-mL volumetric flask. The amorphous silica was filtered out by a Whatman #42 filter paper (Whatman Ltd., Maidstone, UK) before ICP-AES determination for Al, Fe, Ca, Mg, K, S, and B. For total Si analysis, a separate sample of 0.025 g was fused with 0.5 g of Na_2O_2 before being extracted into 500 mL of 0.4 *M* HCl. Total inorganic and organic C were determined by CO_2 coulometry (UIC Corporation, Joliet, IL; Trade names are provided for the benefit of the readers and do not imply endorsement by the EPA and USDA).

X-ray diffraction (XRD) mineralogical evaluation of materials generally followed established procedures (Moore and Reynolds, 1997). Subsamples of the Na-saturated clay (<2 μm) and fine-silt (2–20 μm) size fractions that were separated previously from samples by sedimentation, were subsequently saturated with Mg or K by washing with 0.5 *M* $MgCl_2$ or 0.5 *M* KCl. Excess salts were removed by washing the fractions repeatedly with DI water before air-drying. Ethylene glycol solvation of Mg-saturated samples was run to compare diffraction patterns with air-dried preparation for smectite identification. Subsamples of the K-saturated materials were heated to 550°C and then examined by XRD to differentiate between kaolinite and chlorite. X-ray diffraction examination was performed on oriented samples mounted on glass slides using a Philips diffractometer with Cu-Kα radiation at 40 kV and 15 mA and a LiF monochromator (Philips Electronic Instruments, Mount Vernon, NY). The clay fraction separated from a Georgia palygorskite (Ward's Natural Sci. Establishment, Inc., Rochester, NY) was also examined. Specific surface areas of materials were determined using a single-point Brunauer-Emmett-Teller (BET) N_2 adsorption isotherm on a Quantachrome Quantasorb Jr. surface area analyzer (Quantachrome Corp., Syosset, NY).

Twelve grams of the separated fractions were transferred, in duplicate, into 250-mL polyethylene bottles and to each were added 120 mL of DI water. The samples were placed in a constant temperature chamber at 25 ± 0.5°C. The target pHs of the suspensions were 5, 7, and 9, adjusted with 1.0 *M* HCl or NaOH. The pH adjustment was performed daily for the first 5 d and then twice weekly for most samples afterwards. The pH of the suspensions was maintained within 0.2 units between adjustments, except serpentine samples, which exhibited larger fluctuations of pH for the target pH levels of 5 and 7. The suspension pH was always adjusted to within 0.1 units of the target pH 1 h before sampling. Fifteen milliliters of suspension were taken out for analysis at time intervals of 5, 15, 30, 60, 90, 120, 150, and 180 d. Supernatant solutions were filtered through 0.1-μm Whatman membranes (Whatman Ltd, Maidstone, UK) after centrifugation and before analysis for B, K, Ca, Mg, S, Al, and Si by ICP-AES.

One concern regarding B release behavior is that B release from the structurally incorporated B pool (weathering) into the solution may be complicated by the readsorption of B onto the solids. Presumably there is a threshold level of B in the aqueous solution below which net release occurs, and above which net adsorption occurs. To determine this threshold level, duplicates of 14 separated fractions were equilibrated with boric acid solutions at concentrations of 0, 0.046, 0.092, 0.231, and 0.462 mmol B L^{-1} (1:10, solid/solution) for 12 h at pH 5, 7, and 9, adjusted with 1.0 *M* HCl or NaOH. The suspensions were centrifuged and supernatants filtered and analyzed for B by ICP-AES.

Mineral weathering releases cations into solution and the total amount of each cation released to the solution must be corrected for cation exchange. The cation-exchange capacity (CEC) of separated materials was determined by the method of Polemio and Rhoades (1977). A selectivity of 1.0 for Ca-Mg exchange on illites, shales, and soils was used since Chi et al. (1977) showed that the Ca-Mg isotherms are symmetrical for the soil illites and illites are the dominant clay minerals in the shales and soils used in this study. Only Ca-Mg exchange was considered as the starting materials were saturated with Ca, and as K and Na were not present at sufficient concentrations in the solution to cause significant Na-Ca and K-Ca exchange. The total release of Mg thus includes the Mg in the solution and on the exchange sites.

A chemical equilibrium speciation program MINTEQA2 (Allison et al., 1990) was used to evaluate possible solid phases that may be controlling the solution composition. The evaluation should be seen as an approximation because total dissolved concentrations of Al and Si were used in the calculation.

RESULTS AND DISCUSSION

Short-term Batch Extraction and Particle-Size Separation

Large variations were observed in the cumulative B extracted on a surface area basis as a function of the number of extractions, with maximum extraction from Twisselman clay loam, followed by Traver silt loam, and minimum extraction from Salt Creek shale (Fig. 1). Soluble B is relatively removed rapidly from the materials by the 1:10 extraction procedure. Boron extraction rates appear to approach a low, constant value during the later extractions. More B was extracted from the weathered serpentine than from the fresh serpentine. Selected characteristics of the saturated extracts of two soils show large differences, except for pH, as compared with those studied by Peryea et al. (1985a) for the same soil series (Table 1), suggesting either spatial and/or time variability in the solution chemistry of these soils.

Table 2 presents total chemical analysis of extensively extracted, Ca-saturated size fractions of materials. Insufficient quantities of the clay-size fractions were obtained for both fresh and weathered serpentines, and thus they were not used in the weathering study. The clay fraction that exhibited greater surface area also contained higher total B compared with the fine-silt fraction separated from the same material. Despite extensive extraction with dilute $CaCl_2$ solution, large amounts of residual B were not removed. This residual B is likely structurally incorporated or occluded within the minerals. The remaining pool of surface adsorbed B is likely low. Both total inorganic and organic C were low and their contribution to the total residual B are likely insignificant. The B/Mg molar ratios in the clay-size fraction were lower than those in the fine-silt fraction, except Moreno Gulch shale for which the opposite is observed. Significant amounts of S, presumably in the

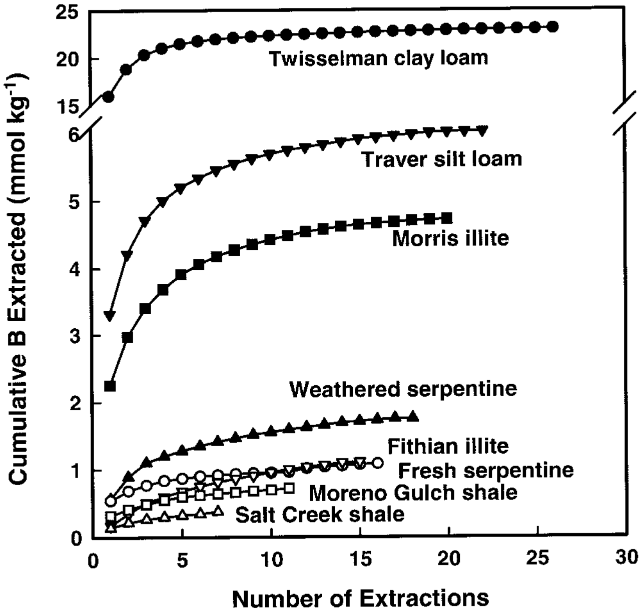

Fig. 1. Cumulative B extracted as a function of sequential extractions (12 h, 1:10 w/v with 0.1 *M* $CaCl_2$ for the first three extractions and 0.01 *M* $CaCl_2$ for subsequent extractions). The specific surface areas were as follows: Twisselman clay loam (<250 μm), 31 m^2 g^{-1}; Traver silt loam (<250 μm), 27 m^2 g^{-1}; Morris illite (<50 μm), 62 m^2 g^{-1}; Weathered serpentine (<50 μm), 38 m^2 g^{-1}; Fithian illite (<50 μm), 52 m^2 g^{-1}; Fresh serpentine (<50 μm), 18 m^2 g^{-1}; Moreno Gulch shale (<250 μm), 30 m^2 g^{-1}; and Salt Creek shale (<250 μm), 75 m^2 g^{-1}.

Table 1. Selected characteristics of unreclaimed surface soils showing the mean and sample standard deviation values ($n = 2$).†

Soil	Saturation percentage	24-h Saturation extract pH	EC	SAR	B
	%		dS m^{-1}	mmol L^{-1}	
Traver silt loam	**53.8 ± 2.5**	**8.4 ± 0.1**	**38 ± 2**	**196 ± 12**	**2.31 ± 0.16**
Twisselman clay loam	**49.5 ± 2.8**	**8.1 ± 0.1**	**72 ± 3**	**215 ± 11**	**14.7 ± 0.80**

† EC, electrical conductivity; SAR, sodium adsorption ratio $\{[Na^+]/(0.5[Ca^{2+} + Mg^{2+}])^{0.5}\}$.

form of sulfides, were observed in the specimen illites and the shales, reflecting the influence of past, reducing conditions on the chemical composition of these materials.

Short-term Adsorption Isotherms

The 12-h B adsorption isotherms at pH 5, 7, and 9 show that there was no measurable B readsorption for all 14 separated fractions (data not shown). The reaction of B was a complete release process. Therefore, no correction for readsorption is necessary for the amount of B released as measured by B concentration in the aqueous solution in the long-term 180-d weathering experiment. This is probably because all the starting materials were high in B even after extensive batch extractions (Table 2) thus a net release of B due to mineral weathering occurred. Washing with DI water for short periods of time is believed to result mainly in desorption of B rather than release of B from mineral weathering, which is a much slower process.

Long-term B Release from Illites

Illite is deficient in interlayer K in comparison with well-crystallized dioctahedral muscovite, which contains 10% K_2O. Morris illite contained more B than Fithian illite (Table 2). The location of B is likely in the tetrahedral layer, as determined in synthetic micas and saponites (Stubican and Roy, 1962). Both illites contain significant amounts of total S with more S in the fine-silt fraction than the clay fraction, probably present as Fe sulfides and organic-bound forms.

Figure 2 presents the B concentration and B release rate as affected by particle size, pH, and time for the two specimen illites. The B release rate is expressed as the difference in the amount of B in solution between two adjacent sampling time periods divided by the sample surface area, and plotted at the mean time of the two sampling events, that is, 10, 22.5, 45, 75, 105, 135, and 165 d. The B release rate between time zero and 5 d was ignored because it was orders of magnitude higher for most samples relative to the rates for the longer time periods, and we were more interested in the long-term weathering rates. For each particle-size fraction, both B concentration and release rate were in the order: pH 5 > pH 7 > pH 9. The B concentrations increased with increasing time; whereas, B release rates decreased with increasing time. Morris illite exhibited higher B concentration in the solution (Fig. 2a) and greater B release rate (Fig. 2b) than did Fithian illite (Fig. 2c,d) for the same size fraction at the same pH. These data are consistent with the greater total B present in Morris illite as compared with Fithian Illite (Table 2). For example, at pH 5 the final B concentrations were 0.056 and 0.042 mmol L^{-1}, respectively, for the <2 μm Morris illite and Fithian illite fractions (Fig. 2), corresponding to a ratio of 1.33. The corresponding solid phase ratio of B in Morris and Fithian illites was 1.40 (Table 2). These similarities in release rates suggest a similar B source in the two illites.

Figure 3 shows the concentrations of Mg, Si, and K, and B/Mg molar ratios of release for Morris illite. Similar results were also observed for Fithian illite. Magnesium concentrations increased with time and decreased with increasing pH. At pH 5 and 7, reaction of the fine-silt fraction resulted in a higher Mg concentration than did reaction of the clay-size fraction. This result occurred despite the fact that the fine-silt fraction had a lower percentage of MgO in the solids compared with the clay-size fraction (Table 2). Since all the starting

Table 2. Total chemical compositions of extensively extracted, Ca-saturated fractions. The mean percentage of components were based on 110°C oven dry mass ($n = 2$).

Sample	Surface area	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	SO_3	H_2O	SUM	B	B/Mg Molar	Total C Organic	Inorganic
	m^2 g^{-1}	%									mmol kg^{-1}	ratio	g kg^{-1}	
Morris illite (<2 μm)	**93**	**55.4**	**22.6**	**4.80**	**0.90**	**2.07**	**5.52**	**0.24**	**7.73**	**99.3**	**28.0**	**0.0544**	**1.9**	**0.06**
Morris illite (2–20 μm)	**47**	**63.7**	**15.3**	**5.61**	**0.49**	**1.24**	**3.80**	**2.71**	**5.67**	**98.5**	**19.5**	**0.0632**	**1.4**	**0.69**
Fithian illite (<2 μm)	**88**	**49.4**	**24.1**	**6.56**	**1.23**	**2.24**	**5.50**	**0.26**	**7.75**	**97.0**	**20.0**	**0.0359**	**9.7**	**0.04**
Fithian illite (2–20 μm)	**17**	**69.4**	**11.8**	**4.43**	**0.32**	**0.99**	**2.52**	**3.06**	**6.45**	**99.0**	**10.4**	**0.0423**	**12**	**0.03**
Fresh serpentine (2–20 μm)	**23**	**37.7**	**1.97**	**10.1**	**1.99**	**34.7**	**0.01**	**0.08**	**12.7**	**99.3**	**12.1**	**0.0114**	**0.5**	**2.00**
Weathered serpentine (2–20 μm)	**39**	**38.0**	**1.17**	**6.46**	**1.10**	**38.5**	**0.01**	**0.08**	**12.8**	**98.1**	**7.95**	**0.0129**	**0.6**	**1.00**
Salt Creek shale (<2 μm)	**67**	**67.8**	**13.4**	**2.96**	**1.10**	**1.02**	**0.94**	**0.33**	**10.8**	**98.4**	**9.31**	**0.0163**	**21**	**<0.004**
Salt Creek shale (2–20 μm)	**75**	**78.1**	**8.6**	**1.49**	**0.49**	**0.50**	**1.21**	**0.26**	**7.45**	**98.1**	**5.06**	**0.0201**	**8.2**	**<0.004**
Moreno Gulch shale (<2 μm)	**44**	**60.5**	**17.4**	**4.26**	**1.72**	**1.89**	**1.17**	**0.39**	**12.6**	**99.9**	**14.1**	**0.0014**	**23**	**<0.004**
Moreno Gulch shale (2–20 μm)	**23**	**67.4**	**15.6**	**2.68**	**1.28**	**1.04**	**2.73**	**0.37**	**7.76**	**98.9**	**9.74**	**0.00083**	**13**	**<0.004**
Traver silt loam (<2 μm)	**90**	**44.6**	**18.7**	**9.77**	**1.85**	**8.27**	**3.37**	**0.13**	**10.8**	**97.5**	**23.3**	**0.0368**	**5.7**	**0.38**
Traver silt loam (2–20 μm)	**5.7**	**61.6**	**15.6**	**4.46**	**2.09**	**2.52**	**3.14**	**0.08**	**7.90**	**97.4**	**8.08**	**0.0408**	**3.4**	**0.05**
Twisselman clay loam (<2 μm)	**126**	**54.7**	**16.2**	**9.11**	**2.40**	**5.51**	**2.59**	**0.13**	**8.66**	**99.3**	**22.3**	**0.0300**	**9.4**	**0.22**
Twisselman clay loam (2–20 μm)	**6.8**	**68.8**	**13.6**	**2.97**	**2.23**	**1.38**	**2.21**	**0.09**	**6.18**	**97.5**	**6.86**	**0.0378**	**5.9**	**0.02**

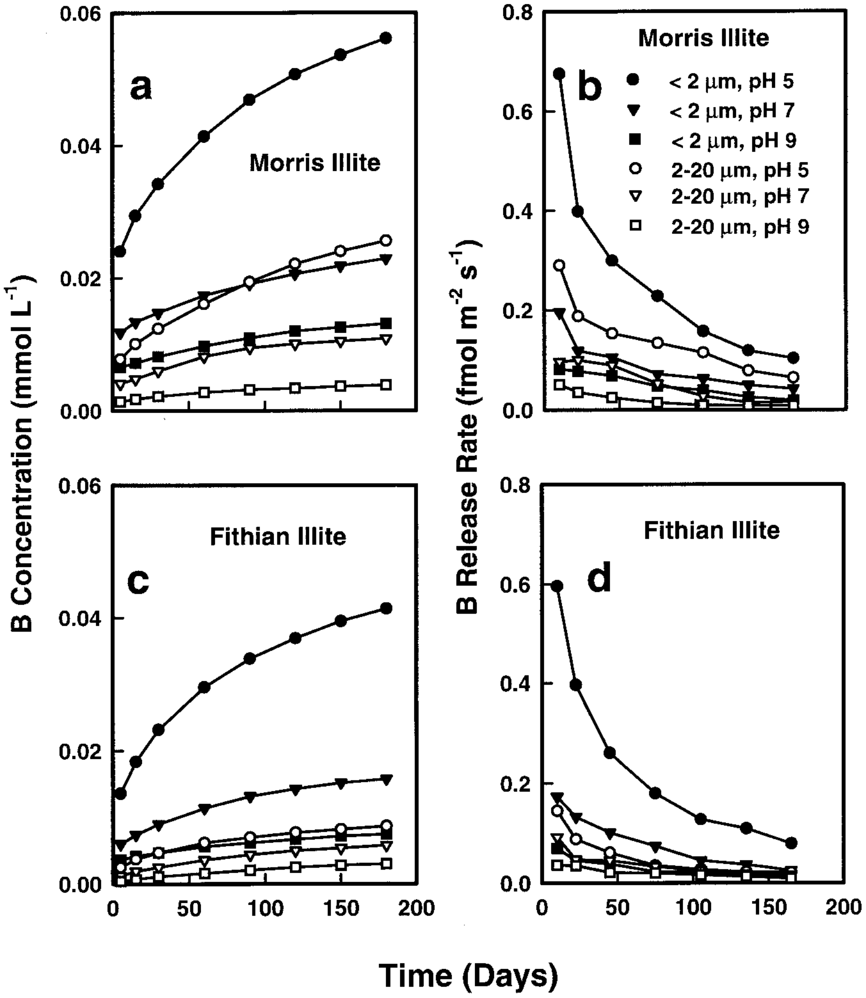

Fig. 2. Effects of particle size, pH, and time on (a) B concentration and (b) B release rate for Morris illite, and (c) B concentration and (d) B release rate for Fithian illite. The B release rate is expressed as the difference in the amount of B in solution between two adjacent sampling time periods divided by the sample surface area, and plotted at the mean time of the two adjacent sampling events, excluding time zero and 5 d, that is, 10, 22.5, 45.75, 105, 135, and 165 d.

materials were saturated with Ca, the Mg and K in the solution must have come from the dissolution of the mineral structure. The molar ratio of B/Mg of release, thus could serve as an indication of the nature of the dissolution reaction. If illites dissolve stoichiometrically, then elemental ratios of release, such as B/Mg must be the same as the B/Mg ratio in the solid phase. Figure 3b clearly shows that Morris illite dissolved nonstoichiometrically at all pHs. The B/Mg ratios of release were generally smaller than the B/Mg ratios in the solids except for the clay fraction at pH 5 (Table 2). This suggests that Mg is preferentially released into the aqueous solution phase relative to B.

The behavior of Si concentration as a function of time (Fig. 3c) suggests that Si concentration cannot be used as a meaningful weathering indicator for our purpose. No attempt was made to use B/Si ratio of release to characterize weathering since Si release was complicated by second phase precipitation and adsorption-desorption. Calculations using MINTEQA2 chemical equilibrium speciation program show that the solutions were supersaturated with respect to gibbsite, halloysite, and kaolinite at pH 5, 7, and 9 for Morris illite-clay fraction. The convergence of Si concentrations at pH 5 for both size fractions indicates a steady state of the mineral–water interaction; however, the K concentration increased with increasing time at pH 5 (Fig. 3d). Since K resides exclusively in the interlayer of illites, its increase in the solution may be caused by both dissolution of illite particles and Mg displacement of interlayer K.

Long-Term Boron Release from Serpentine

Both fresh and weathered serpentine materials were identified by XRD as antigorite with magnetite as a minor component. Although serpentine has an ideal formula as $Mg_3Si_2O_5(OH)_4$, in natural serpentines there is the possibility for substitution of Al^{3+}, Fe^{3+}, and Fe^{2+} ions, for Mg^{2+} in octahedral coordination, and Al^{3+}, Fe^{3+}, and B^{3+} for Si^{4+} in tetrahedral coordination (Page, 1968). Chemical analysis of serpentine materials (Table 1) is consistent with the chemical composition of antigorites reported by Whittaker and Wicks (1970), who

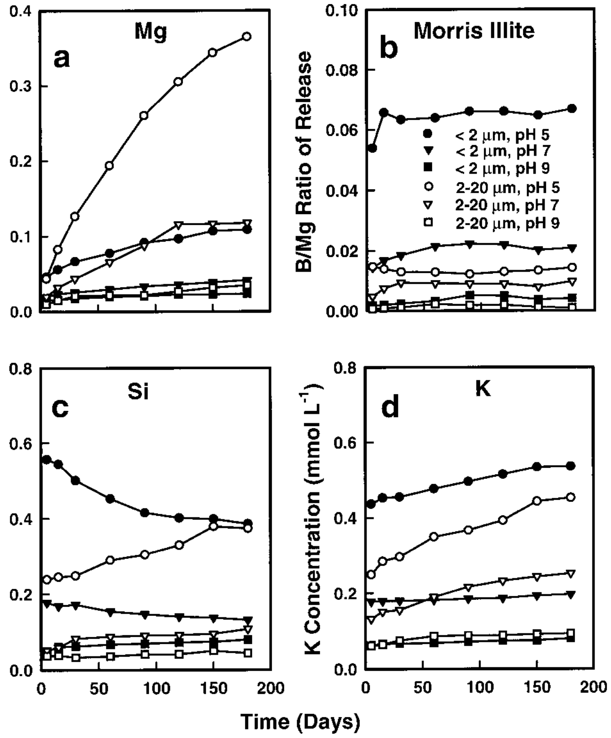

Fig. 3. Effects of particle size, pH, and time on (a) Mg concentration, (b) B/Mg molar ratio of release, (c) Si concentration, and (d) K concentration for Morris illite. The cation-exchange capacity (CEC) was 30.2 and 18.5 cmmol(+) kg^{-1} for the <2- and 2- to 20-μm fractions of Morris illite, respectively.

showed that antigorites have a higher SiO_2 content and a lower MgO and structural H_2O content than the other serpentine minerals (lizardites and chrysotiles). Serpentinization of peridotite rocks in the oceanic crust is accompanied by B enrichment. The mechanism by which B is taken up by oceanic serpentinites is not clear; a relationship exists between temperature of serpentinization of ultramafic rocks of mantle derivation, mineralogy of the serpentinites and their B content. The temperature of serpentinization is inversely related to the B content of the serpentinites, suggesting that B is acquired by the serpentinites from seawater at low temperature (Bonatti et al., 1984).

Greater B concentrations in solution were obtained after reaction of fresh serpentine as compared with weathered serpentine (Fig. 4a), consistent with the higher total B content in the fresh serpentine material (Table 2), and greater extraction of B for the fresh vs. weathered (on a surface area basis) (Fig. 1). Boron release rates were also greater for the fresh serpentine as compared with the weathered serpentine. The B/Mg molar ratio of release were 0.00074 ± 0.00019 at pH 5, 0.00085 ± 0.00011 at pH 7, and 0.00025 ± 0.00048 at pH 9 for the 5- to 180-d time period for the fresh serpentine material, and 0.00048 ± 0.00010 at pH 5, 0.00040 ± 0.00014 at pH 7, and 0.00211 ± 0.00037 at pH 9 for the weathered serpentine material. These values were all lower than the values of 0.0114 and 0.0129 for the starting fresh and weathered serpentine solid phases (Table 2). Again, the dissolution of serpentine is not stoichiometric; Mg is preferentially released into the aqueous solution phase relative to B.

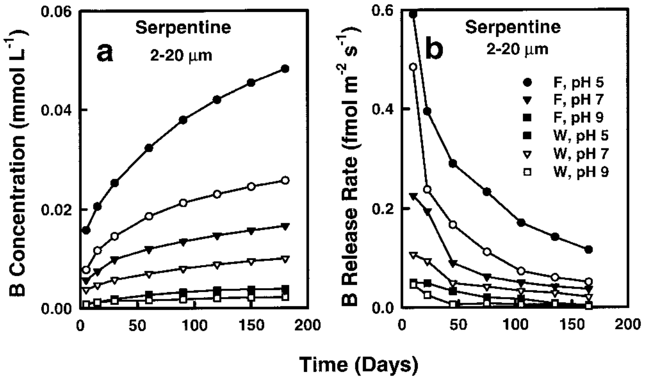

Fig. 4. Effects of pH and time on (a) B concentration and (b) B release rate for both fresh (F) and weathered (W) serpentine (antigorite).

The Si concentration increased with time and decreasing pH. At 180 d and pH 5, Si concentrations ranged from 10 to 19 mg Si L^{-1}. The Si concentrations were in the order: pH 5 > pH 7 > pH 9. Magnesium from the octahedral sheets was released more rapidly than was Si from the tetrahedral sheets, that is, the dissolution was incongruent, consistent with the findings of Lin and Clemency (1981) in a 49-d, pH 6 to 7, dissolution experiment. The B/Si molar ratios in the solution were 40 to 100 times of those in the starting solid phase of fresh serpentine, and 40 to 400 times of those in the starting weathered serpentine solid phase. Thus, the tendency of elemental release from antigorite materials followed the order: Mg > B > Si.

A stability diagram developed from the apparent standard free energy of three California serpentines indicates that a serpentine mineral is unstable at pH < 7 in 0.1 *M* Mg^{2+} solution (Wildman et al., 1971). Serpentine is unstable in the range of pH and Mg^{2+} and H_4SiO_4 activities encountered in most soils. No other crystalline solid phases were detected by XRD at the end of the experiment, and all solutions were undersaturated with respect to serpentine and amorphous silica. Reaction of serpentine resulted in almost steady Si concentration from 5 to 180 d, despite continued increase in Mg concentration in solution. No direct evidence was obtained from this study nor in a study by Wildman et al. (1968) to show that Fe and Al from the structure of serpentine minerals recombine with H_4SiO_4 to form an Fe-rich montmorillonite; however, montmorillonite was found in the soils developed on serpentine parent materials (Wildman et al., 1968). Nevertheless, the presence of Fe and Al in small amounts in the serpentinite and the reverse trend found in montmorillonite, suggest that it is plausible, in the long-term (many years) for complete disruption of the serpentine lattice, resulting in formation of Fe-rich montmorillonite with reconstitution of the dissolution products in quite different proportions (Wildman et al., 1968). Furthermore, B in the weathering products of montmorillonite can be inherited from parent serpentine material and B release rate from serpentine and the solution composition will dictate the content of B in montmorillonite.

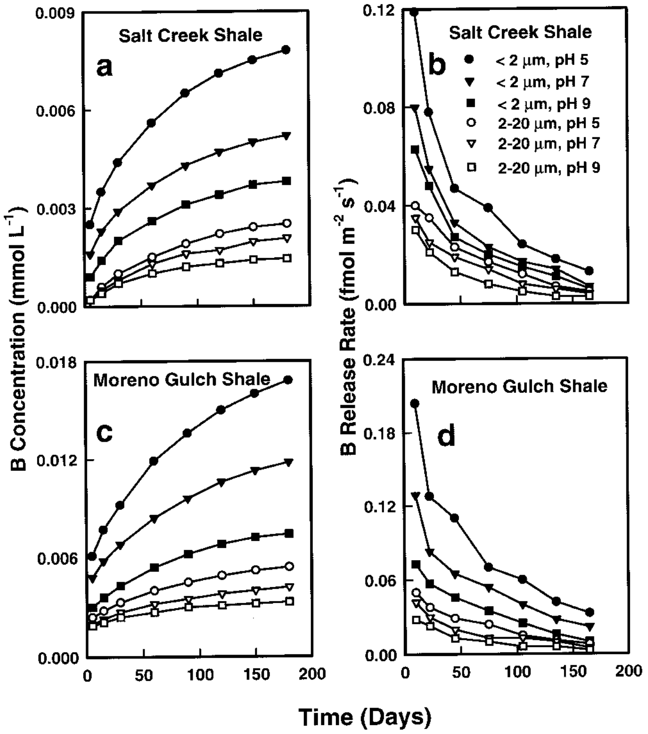

Fig. 5. Effects of particle size, pH, and time on (a) B concentration and (b) B release rate for Salt Creek shale, and (c) B concentration and (d) B release rate for Moreno Gulch shale.

Long-Term Boron Release from Shales

For both shale materials, B concentrations in the solution increased with increasing time and were greater for the clay fractions than for the fine silt fractions (Fig. 5a,c), in agreement with the distribution of B content in the starting size fractions (Table 2). The B release rates (Fig. 5b,d) decreased with increasing time on a surface area basis. Lower B release rates (fmol m^{-2} s^{-1}) were observed for the shales compared with the specimen illites. Unlike specimen illites, Si concentrations in the solution increased with increasing time at all pHs; however, all the solutions were oversaturated with respect to halloysite, gibbsite, and kaolinite for all shale materials at all pHs based on calculations using MINTEQA2 program (Allison et al., 1990). The B/Mg molar ratios of release were lower than the B/Mg ratios in the starting solid phases, again indicating nonstoichiometric dissolution with preferential release of Mg over B.

The high oceanic concentration of B (average 0.416 mmol L^{-1}) results in a correspondingly high content in marine sediments (>10 mmol kg^{-1}); whereas, in nonmarine argillaceous sediments the B content is generally at least one order of magnitude lower (Goldberg and Arrhenius, 1958). Goldberg and Arrhenius (1958) noticed that only a minor fraction, roughly corresponding to the amount dissolved in the interstitial solution, is removed when the pelagic clay sediments are washed with DI water. Less than 10% of the remaining B is removed by exchange of sorbed ions. The major B fraction thus appears to be relatively strongly bonded in the authigenic minerals of the sediment. A large fraction of the B resists dissolution on boiling in 0.1 *M* HCl, but is released on boiling in NaOH, suggesting that B is proxying for Si in the tetrahedral sheets of the clay minerals. Substitution of B for Si is also shown to be possible in a broad range of primary silicates (Christ, 1965) and allophane (Su and Suarez, 1997).

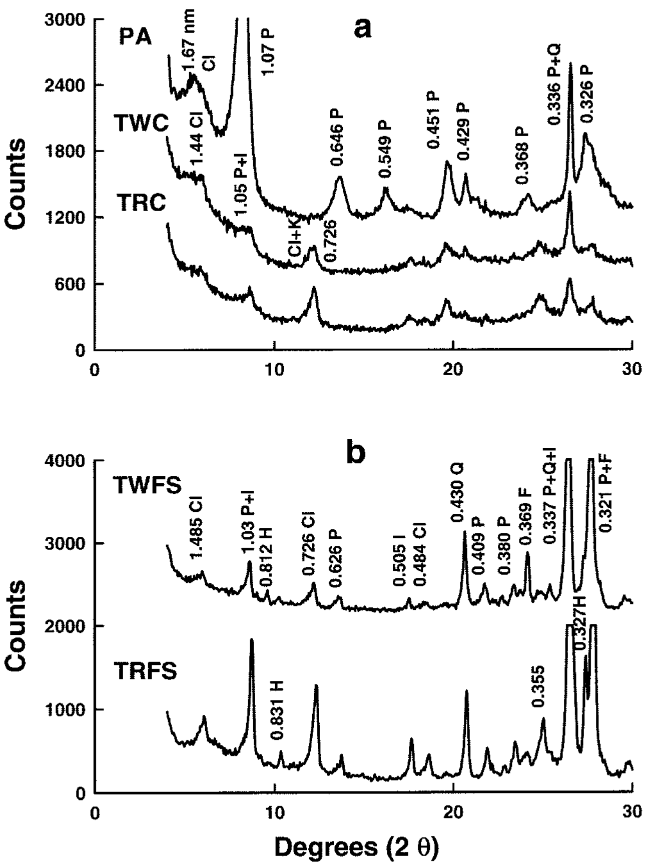

Fig. 6. X-ray diffractograms of Mg-saturated and air-dried (a) Georgia palygorskite (PA), clay-size fractions of Twisselman clay loam (TWC) and Traver silt loam (TRC), and (b) fine-silt size fractions of Twisselman clay loam (TWFS) and Traver silt loam (TRFS). Cl = chlorite, F = feldspar, H = hornblende, I = illite, K = kaolinite, P = palygorskite, Q = quartz.

Long-Term Boron Release from Soil Fractions

The predominant minerals in the clay fractions of both soils were illite, palygorskite, chlorite, and kaolinite (Fig. 6a); whereas, the fine-silt fractions contained illite, palygorskite, chlorite, hornblende, feldspar, and quartz (Fig. 6b). Palygorskite is found in arid and semiarid soils, and is one of the few useful palaeoclimatic indicators among the clay minerals (Singer, 1980, 1984). The intensities and peak sharpness for the soil palygorskites vary and probably are related to the proportion and crystallinity of palygorskite in the soil samples. The conditions of formation of palygorskite include alkaline pH, high Si and Mg, and low Al activity, and most data suggest neoformation rather than diagenesis (Singer, 1979). Although widespread in arid soils, palygorskite has not been reported for the two soils used in this

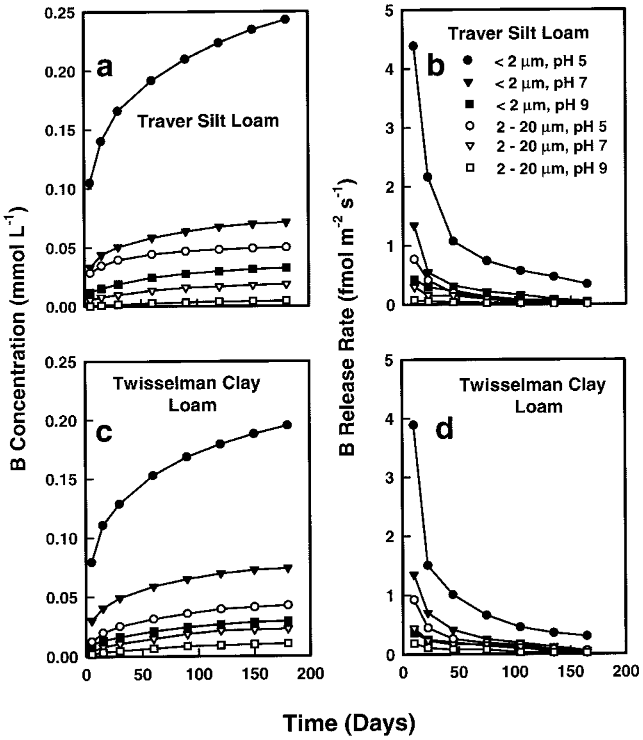

Fig. 7. Effects of particle size, pH, and time on (a) B concentration and (b) B release rate for Traver silt loam, and (c) B concentration and (d) B release rate for Twisselman clay loam.

study. We show below that palygorskite had a pronounced effect on B release.

Although the total B contents in both size fractions of the soils were lower than those in the Morris illite (Table 2), both B concentrations in the solution (Fig. 7a,c) and B release rates (Fig. 7b,d) for each fraction separated from both soils were greater at all pH's relative to Morris illite. Titration of the clay fraction suspension to pH 5 for 5 d, and to pH 7 for 30 d resulted in B concentrations that were in the toxic range for plant growth, despite the extensive leaching of all materials before titration. Soil acidification in a field at a moisture content near the field capacity (matric potential of -33 kPa), such as may occur during reclamation, on addition of sulfuric acid, may result in B concentrations several times greater than the B concentration of a 1:10 (w/v) soil suspension, causing severe toxicity consequences to plants.

To identify the mineral sources for B in the samples taken from the Traver silt loam and Twisselman clay loam, we first examined the solution compositions of the soils and specimen illites. A comparison of Fig. 8 and 3 shows that: (1) higher Mg and Si were released from Traver silt loam (and from Twisselman clay loam, data not shown) than from Morris illite at pH 5 and 7, with Si concentration in solution approaching the solubility of amorphous silica with increasing time in the clay-size fraction of Traver silt loam at pH 5; (2) The anomalously large Mg release at pH 5 cannot be explained by illite dissolution, assuming the soil illite has similar Mg content, mineralogical structure, and dissolution behavior as the specimen Morris illite; (3) the B/Mg molar ratios of release for the soil fractions were always less than those in the starting materials (Table 2), indicating nonstoichiometric dissolution; (4) K concentration in the solution for Traver silt loam and Twisselman clay loam were lower than those for Morris illite, consistent with a lower content of total K_2O in the soil fractions (Table 2). In addition, Fig. 9 shows that the cumulative HCl consumption for maintaining pH 5 was greater for the clay fractions of soils than for

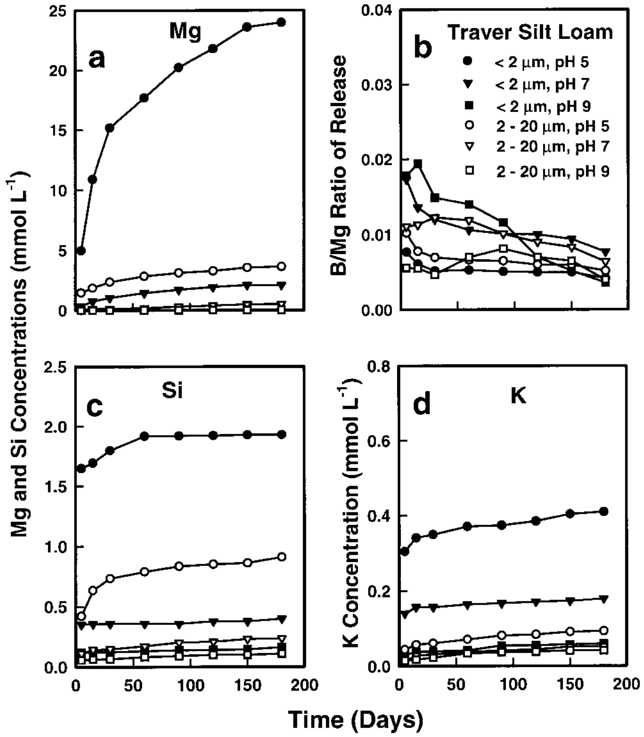

Fig. 8. Effects of particle size, pH, and time on (a) Mg concentration, (b) B/Mg molar ratio of release (c) Si concentration, and (d) K concentration for Traver silt loam. The cation-exchange capacity (CEC) was 38.0 and 6.99 cmmol(+) kg^{-1} for the <2- and 2- to 20-μm fractions of Traver silt loam, respectively.

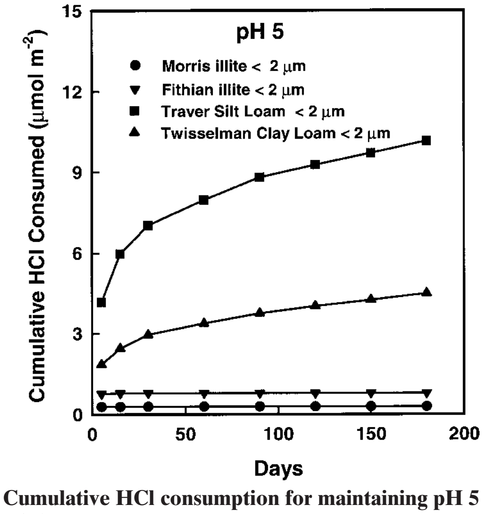

Fig. 9. Cumulative HCl consumption for maintaining pH 5 as a function of time.

Table 3. Average B release rates (fmol m^{-2} s^{-1}) and sample standard deviations from 150 to 180 d for the separated fractions ($n = 2$).

Sample	Particle size	pH 5	pH 7	pH 9
	μm			
Morris illite	<2	0.104 ± 0.002	0.043 ± 0.003	0.020 ± 0.002
Morris illite	2–20	0.065 ± 0.003	0.017 ± 0.002	0.009 ± 0.001
Fithian illite	<2	0.079 ± 0.002	0.025 ± 0.002	0.013 ± 0.001
Fithian illite	2–20	0.021 ± 0.001	0.016 ± 0.001	0.009 ± 0.001
Fresh serpentine	2–20	0.116 ± 0.006	0.037 ± 0.003	0.004 ± 0.000
Weathered serpentine	2–20	0.051 ± 0.004	0.021 ± 0.001	0.002 ± 0.000
Salt Creek shale	<2	0.013 ± 0.001	0.007 ± 0.001	0.006 ± 0.000
Salt Creek shale	2–20	0.005 ± 0.000	0.004 ± 0.000	0.003 ± 0.000
Moreno Gulch shale	<2	0.033 ± 0.003	0.022 ± 0.002	0.010 ± 0.001
Moreno Gulch shale	2–20	0.008 ± 0.000	0.005 ± 0.000	0.003 ± 0.000
Travel silt loam	<2	0.342 ± 0.027	0.060 ± 0.006	0.044 ± 0.004
Traver silt loam	2–20	0.035 ± 0.003	0.025 ± 0.002	0.012 ± 0.001
Twisselman clay loam	<2	0.300 ± 0.022	0.058 ± 0.005	0.037 ± 0.003
Twisselman clay loam	2–20	0.058 ± 0.004	0.031 ± 0.002	0.025 ± 0.002

the clay fractions of specimen illites. It is, therefore, concluded that B release cannot be explained by illite weathering alone. Boron release is likely associated with a Mg-rich mineral, namely palygorskite.

Table 3 summarizes the average B release rates from 150 to 180 d time period for all the separated fractions. It is clear that B release is related to mineralogy, inversely related to particle size and pH (for pH < 9). Time is an additional factor as discussed in the previous sections.

Little has been done to fractionate B in arid and semiarid soils. Jin et al. (1987) separated soil B in 14 soils of the eastern USA into seven fractions: water soluble, 0.02 *M* $CaCl_2$ extractable, mannitol extractable, acidified $NH_2OH.HCl$ extractable, ammonium oxalate in the dark (pH 3.25) extractable, ammonium oxalate under ultraviolet light extractable, and residual B. They found that B concentration in corn (*Zea mays* L.) tissue is correlated positively with water soluble, $CaCl_2$–extractable, mannitol-extractable, and acidified $NH_2OH.HCl$-extractable B. The sum of these four fractions, which are related to B availability, accounts for only 0.4 to 2.0% of the total B in soils. Boron in noncrystalline and crystalline Al and Fe oxides and silicates is relatively unavailable for plant uptake. In the soils containing palygorskite, B behavior is expected to be different from that in acidic soils. Boron associated with palygorskite may be readily released into soil solution when the soil pH is decreased. Thus, any B fractionation scheme for arid zone soils should take this into account.

No attempt was made in the present study to evaluate the role of organic matter in B release. A previous study showed that between 2 to 23% of total B is in organically bound forms (0.02 *M* HNO_3 + 30% H_2O_2 extractable) in 24 Ontario, Canada soils (Hou et al., 1994). The contribution to B release during the 180-d experiment from the organically bound forms of B in this study is probably not significant due to the low organic C content (Table 2), and repeated extraction with dilute $CaCl_2$ solution before the weathering experiment. Also, organically bound B is less important in high total B soils. Assuming that maximum B adsorption capacity of humic acids is 200 mmol B kg^{-1} at pH = 9 and 40 mmol B kg^{-1} at pH = 7 (Gu and Lowe, 1990), then the maximum organic B would be <18% of the total B at approximately pH 9 and <4% of the total B at approximately pH 7 for the separated soil fractions of Traver silt loam and Twisselman clay loam. Since the B concentration in the soil solution is usually much less than the B concentration for the maximum B adsorption, the organically bound B out of total B would be <10% of the total B. The organic contribution of B adsorption-release in our experiments has thus been neglected, due to the low organic C content and rapid mineralization of organic matter in the arid soil environment, as well as the high B content of these soils.

Estimation of long-term release rates can be used for predicting B concentration in the field. If we assume the final B release rates in Table 3 are the steady-state rates, then after 100 yr, Traver silt loam (<2 μm) fraction will release 1.1 μmol m^{-2} at pH 5, 0.19 μmol m^{-2} at pH 7, and 0.14 μmol m^{-2} at pH 9. To reach a toxic level of 0.5 mmol B L^{-1} if a soil moisture content of 50 g kg^{-1} is maintained in the field, the time needed is 0.25 yr at pH 5, 1.5 yr at pH 7, and 2 yr at pH 9. Consequently, B regeneration is not likely to affect irrigated soils if sufficient leaching is maintained but it will have an adverse impact on non-irrigated areas.

CONCLUSIONS

Despite extensive extraction with dilute $CaCl_2$ solution to decrease the solution B concentration to <0.001 mmol L^{-1} before separation of particle size, appreciable amounts of B were released from both the clay and fine-silt fractions of all materials through nonstoichiometric dissolution. Boron release rate decreased with time and pH and was a function of particle size and mineralogy. At each pH for each particle-size fraction, B release rate was in the order: Traver silt loam > Twisselman clay loam > fresh serpentine > Morris illite > Fithian illite > weathered serpentine > Moreno Gulch shale > Salt Creek shale. Illite, chlorite, and palygorskite were identified in the clay and silt fractions of the soils. Boron release was accompanied with high Mg release in the soils, suggesting palygorskite as a source for B. Boron release from the soils was attributed to a Mg-rich phase, likely palygorskite rather than illite as has been previously assumed. Weathering of soils with a high amount of structurally bound B may result in toxic levels of B within a few years of reclamation unless leaching is maintained.

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