3. The role of silica

The rice plant is among several silica cumulating organisms, including *Equesetum* (horse tails) (Jones and Handreck, 1967), diatoms (Volcani, 1978), sedges (Epstein, 1999) and cedars (*Thuja*) (Weiss and Herzog, 1978). Silicon is after oxygen, the second most abundant element in the earth's lithosphere (Ingri, 1978; Iler, 1978), and its abundance has caused agronomists and nutritionists to overlook its potential metabolic role. It has been regarded as a passive element. However, several studies over the past 40 years have shown its essentiality for a number of organisms including, diatoms, *Equesetum* (Raven, 1983), and for chickens (Carlisle, 1972, 1978; Carlisle et al., 1977), rats (Schwarz, 1978) and probably all other animals. Silicon deficiency in animals promotes failure of normal collagen and results in impaired bone formation (Carlisle, 1978). Recently the question of its essentiality has been raised for higher plants, as well (Epstein, 1994, 1999). Studies show that there are large responses in rice yield and resistance to fungal diseases with adequate silicon nutrition (Mengel and Kirkby, 2001) and from grazing by slugs (Wadham and Parry, 1981). Problems in determination of essentiality are related to development of nutritional environments sufficiently low in silicon (Weiss and Herzog, 1978; Werner and Roth, 1983).

Silica is a structural element in diatoms and a cell wall component in rice and many other grasses but also occurs in vegetative tissues in lesser amounts. Jones and Handreck (1967) divide plants into three categories: those that cumulate large amounts, such as rice, others intermediate with lower levels, including many grasses, and those that seem to limit silica, including legumes and many other dicots, although these plants also respond to adequate levels of silica (Epstein, 1999). The proportion located in vegetable tissues is greater in those species, *i.e.* legumes and some other dicots that do not deposit silica in cell walls, reviewed by Jones and Handreck (1967) and McManus et al. (1977). The exact form and association of this silica is obscure. Distribution and form can be altered by method of preparation (McManus et al., 1977). Scanning electron microscopy has located the major deposits in rice straw epidermal layers which is greater in leaves than stems (Balasta et al., 1989; Agbagla-Dohnani et al., 2003; Ha et al., 1994a,b; Soni et al., 1972; Soni and Parry, 1973).

The plant organisms that cumulate silica do so through active transport and spend one ATP per silicon atom. The cost of synthesizing an equivalent amount of lignin is about 27 ATP (Raven, 1983). The advantages of energy saving by replacement of lignin by silica may have evolutionarily promoted silicification in some plants. Rice is a C3 plant in relatively tropical environments, where competition with more photosynthetically efficient C4 plants may have promoted the evolution of silica uptake. A disadvantage is that the plant is dependent upon availability of soluble silicic acid in soils. Many tropical soils may be depleted in silica. One of the most available forms of silica is biogenic opal from the decay of plant residues (Drees et al., 1989). Alumina and clays reduce silicic acid availability in soil, and quartz itself has a low availability (Jones and Handreck, 1967).

Silica is absorbed in the form of orthosilicic acid, $Si(OH)_4$. The first pK of silicic acid is 9.8 and the second pK at 11.8 (Ingri, 1978), so that the form in the plant sap is not ionized and does not have any buffering action in plant metabolism (Jones and Handreck,

1967; Raven, 1983). Evapotransportation concentrates silicic acid above its saturation which promotes polymerization into insoluble polysilicic acids that deposit in exterior plant cell walls of grasses. Jones and Handreck (1967) indicated that the crystalline form is that of opal. However, they obtained this identification on silica from nitric acid ashed samples. However, nitric acid altered the NIR spectra of phytolithic silica, and reduced its solubility (Van Soest and Lovelace, 1969; Van Soest et al., 1971). Plant silica has a considerable solubility in hot neutral-detergent, which may represent a separate phase from that which is less soluble (Shen et al., 1998a). Hot water extraction curves also indicate two phases in rice straw (Van Soest and Lovelace, 1969). There may be more than one chemical form of silica in rice and other plants.

While most of the silica in rice straw appears to be in the plant cell wall it is obvious that there is some soluble. The levels in plant sap can greatly exceed that of the soil solution, indicating active transport. Concentrations of 400–800 ppm as SiO_2 have been reported in xylem sap of rice (Jones and Handreck, 1967). These levels of soluble silica exceed the saturation of silicic acid in distilled water (about 120–140 ppm as SiO_2 at 25 °C) and begs the question as to how it is stabilized and complexed in physiological solutions. Evidence for active transport is suggestive of unidentified organic complexes.

The organic chemistry of silicon parallels that of boron in that like boric acid, silicic acid can form complexes with vicinal phenols and possibly with sugars (Williams, 1978) and complex carbohydrates (Iler, 1978). Perry et al. (1987) examined the deposition of silica associated with polysaccharides in hairs from the lemma of reed canary grass. Type of polysaccharide was associated with ultrastructural form of the silica.

The identification of organically bound silicon in biological tissues is an extremely difficult area of investigation, because of its great geological abundance, and low concentrations of metabolically active silicon. Small amounts of silicon contaminate water, reagent grade chemicals, and variably larger amounts in food and feed, particularly cereals (Weiss and Herzog, 1978; Werner and Roth, 1983). Use of laboratory glassware is a problem, so the background contaminating silicon cannot be easily distinguished from what might be present in a biological preparation.

Silicic acid readily complexes with 1,2-dihydroxybenzenes, such as catechol, caffeic acid, tropolones and tannins which can form spontaneously at room temperature and without enzymes to form 3 mol of diphenol per silicon atom (Weiss and Herzog, 1978). Such complexes are suggested in rice straw (Mengel and Kirkby, 2001). However, Inanaga and Okasaka (1995) and Inanaga et al. (1995) suggest that silicon is bound in lignin-carbohydrate complexes, and lignin synthesis is reduced in silicon deficient plants.

3.1. Silicon and forage digestibility

Van Soest and Jones (1968) reported a depression in digestibility of the oat plant grown hydroponically with different levels of added silica. Smith et al. (1971) reported on eight species of grasses and found that silica depressed organic matter about one unit of organic matter. Later Van Soest (1981) extracted Bermuda grass, reed canary grass, and rice straw with neutral detergent. Considerable silica was dissolved and by using alfalfa as a negative control obtained an increase in NDF digestibility of organic matter per unit of silica removed (Fig. 1).

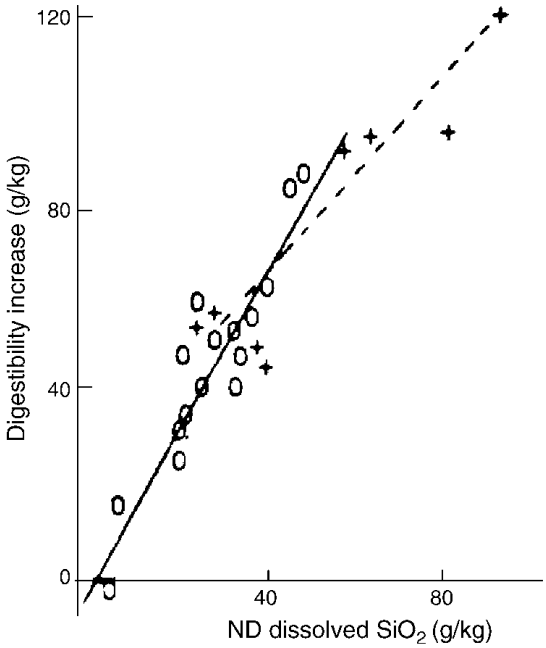

Fig. 1. Increase in digestible amount of NDF organic matter as related to the amount of silica dissolved by neutral detergent. Grasses include rice straw, coastal Bermuda, buffalo grass and reed canary. The doubly extracted samples (+and dotted line) at the top of the figure are primarily rice straws. Single extraction $y = 1.8x - 6.5$; double extraction $y = 1.1x + 17$ (Van Soest, 1981).

Two preliminary reports from the international rice institute (IRRI) in the Philippines indicated no effect of silica upon digestibility of rice straw (Balasta et al., 1988; Khush et al., 1988). However, a final paper by Balasta et al. (1989) obtained significance with an analysis of variance to remove varietal differences. Recalculations of the Balasta et al. (1988) and Khush et al. (1988) data with analysis of variance to remove varietal effects, also gave significance (Table 2). The interactions between varieties is large and works against the relationship of silica with digestibility. The rice plants studied by Khush et al. (1988) (4 varieties and 16 samples) and Balasta et al. (1988) (2 varieties and 10 samples) were grown hydroponically with levels of silica ranging from 0 to 400 ppm in solution. Ten samples (two varieties) are shared in common between Khush et al. (1988) and Balasta et al. (1988), but the paper of Balasta et al. (1989) has independent *in vitro* digestion data also done by the method of Minson and McLeod (1972). Comparison of the organic matter digestibilities between the papers indicate great analytical variation from the same laboratory. Two outliers in the Khush data have been eliminated and values of Balasta et al. (1989) substituted for the calculations in Table 2.

Enishi (2002), Nakashima and Ørskov (1990) and Walli et al. (1988) compared plant parts within varieties of rice straw. There is no observable association in the whole plant data, but when silica is regressed for the plant parts upon their respective digestibilities negative slopes are obtained between silica and digestibility. Nakashima and Ørskov (1990) measured *in vitro* dry matter digestibility (IVDMD) to obtain a negative slope of 1.9. Calculation of the data of Enishi (2002) and Hasan et al. (1993b) indicates an even larger slope of −4.6