Trace Mineral Bioavailability in Ruminants

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ABSTRACT Absorption of selenium and copper is much lower in ruminants than in nonruminants. The low absorption of these minerals in ruminants is due to modifications that occur in the rumen environment. Selenium bioavailability is reduced by high dietary sulfur and the presence of cyanogenic glycosides in certain legumes. Feeding organic selenium from selenomethionine or seleniumized yeast results in much higher tissue and milk selenium concentrations than are obtained with selenite. High dietary molybdenum in combination with moderate to high dietary sulfur results in formation of thiomolybdates in the rumen. Thiomolybdates greatly reduce copper absorption, and certain thiomolybdate species can be absorbed and interfere systemically with copper metabolism. Independent of molybdenum, high dietary sulfur reduces copper absorption perhaps via formation of copper sulfide. High dietary iron also reduces copper bioavailability. Dietary factors that affect bioavailability of zinc in ruminants are not well defined. Phytate does not affect zinc absorption in ruminants because microbial phytase in the rumen degrades phytate. Manganese is very poorly absorbed in ruminants, and limited research suggests that high dietary calcium and phosphorus may reduce manganese absorption. J. Nutr. 133: 1506S–1509S, 2003.

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Efficiency of absorption of many trace minerals and dietary factors that affect bioavailability of minerals differ greatly between ruminants and nonruminants. In ruminants, microbial digestion in the rumen and reticulum precedes mammalian digestion in the abomasum and small intestine. Ruminant diets are usually high in fiber, and considerable digestion of fiber occurs via microbial fermentation in the rumen. However, association of minerals with fiber fractions in feedstuffs (1) and/or binding of minerals to undigested fiber constituents in the gastrointestinal tract may alter bioavailability of some trace minerals in ruminants (2). The pH in the rumen environment is only slightly acidic (6.0–6.8), and in the rumen, many trace minerals exist largely in an insoluble form (3). At least some of the metal complexes that are formed in the rumen remain insoluble even under the acidic conditions found in the abomasum (3). This article briefly reviews dietary factors that affect the bioavailability of selenium, copper, zinc and manganese in ruminants. Differences in the bioavailability of supplemental sources of these metals are also discussed.

Selenium

Absorption of selenium is much lower in ruminants than in nonruminants. Absorption of orally administered $^{75}$Se was only 34% in sheep compared with 85% in swine (4). Low absorption of selenium in ruminants is believed to result from reduction of dietary selenium to insoluble forms such as elemental selenium or selenides in the rumen environment (5,6).

Sulfur. Selenium and sulfur have similar physical and chemical properties, and a number of studies indicate that increasing dietary sulfur reduces the bioavailability of selenium. Sulfate addition to pregnant ewe diets that were low in selenium increased the incidence of white-muscle disease in their lambs (7). After oral administration of $^{75}$Se as sodium selenate, sheep fed a low-sulfur diet (0.5 g of sulfur/kg) excreted less radioactivity in urine and had higher blood $^{75}$Se activity than sheep fed a diet that contained 2.4 g of sulfur/kg (8). Increasing dietary sulfur from 2.1 to 4.0 or 7.0 g of sulfur/kg of diet resulted in a linear decrease in plasma selenium and apparent absorption of selenium in lactating dairy cows (9). Concentrations of selenium in liver and rumen bacteria were also reduced in sheep when dietary sulfur was increased from 2.2 to 4.0 g of sulfur/kg of diet (10).

Type of diet. Incidence of white-muscle disease was higher in lambs fed low-selenium alfalfa hay than in lambs fed grass hay of similar selenium content (11). Selenium absorption and retention were greater in sheep fed a concentrate (barley)-based diet than in those fed a forage (alfalfa hay)-based diet.
(12). Differences in the bioavailability of selenium among forages or between concentrate and forage diets may relate to differences in sulfur content or to the presence of compounds such as cyanogenetic glycosides that are antagonistic to selenium.

**Cyanogenetic glycosides.** Cyanogenetic glycosides are found in certain legumes and can be metabolized to cyanide in the rumen. Ewes fed a white-clover variety that was high in cyanogenetic glycosides had much lower selenium status, assessed by erythrocyte glutathione peroxidase activity, than ewes fed a white-clover variety low in cyanogenetic glycosides (13). Lambs born to ewes fed clover that was high in cyanogenetic glycosides also had greatly reduced erythrocyte glutathione peroxidase activity. It is unclear how cyanogenetic glycosides affect selenium metabolism. However, in rats, cyanide was shown to increase urinary selenium excretion (14).

**Calcium.** Limited research suggests that either high or low dietary calcium may reduce selenium absorption. In nonlactating dairy cows, selenium absorption was maximized with 8.0 g of calcium/kg of diet (15). In this study, reducing dietary calcium to 4.0 g of calcium/kg of diet or increasing dietary calcium to 12.5 g of calcium/kg of diet resulted in an ~50% decrease in selenium absorption. Feeding young calves either extremely low (1.7 g of calcium/kg of diet) or high (23.5 g of calcium/kg of diet) dietary calcium did not significantly affect selenium absorption (16).

**Bioavailability of supplemental sources of selenium.** Most studies indicate that the bioavailability of selenium from selenite and selenate is similar in ruminants (17,18). Organic selenium in selenized yeast results in much larger increases in blood and milk selenium concentrations than selenite (18,19). Lambs fed selenomethionine also had higher selenium concentrations in skeletal muscle and in a number of other tissues than lambs fed selenite (20). Selenomethionine is the predominant form of selenium that occurs naturally in feedstuffs and in selenized yeast. Incorporation of selenomethionine into nonspecific body proteins in place of methionine (21) likely explains the higher selenium concentrations in tissue and milk of ruminants that were fed organic compared with selenite selenium. In most studies, selenium from selenomethionine and selenite was absorbed with similar efficiency (12,20,22). However, urinary excretion of selenium was greater in lambs (20) and goats (22) fed selenite compared with those fed selenomethionine. Selenomethionine and selenized yeast were approximately twice as bioavailable, based on erythrocyte glutathione peroxidase activity, as selenite when fed to selenium-deficient heifers (23).

**Copper**

Copper absorption in ruminants is low (<1.0–10.0%) relative to values reported in nonruminants (24). The low absorption of copper in ruminants is largely due to complex interactions that occur in the rumen environment. Before development of a functional rumen, copper absorption is high (70–85%) in milk-fed lambs but decreases to <10% after weaning (25). It is well documented that copper requirements vary greatly in ruminants depending on concentrations of other dietary components, especially sulfur and molybdenum.

**Molybdenum and sulfur.** A three-way interaction between copper, molybdenum and sulfur has been recognized since the 1950s (26). This interaction can occur with concentrations of molybdenum and sulfur that are seen naturally in feedstuffs and was shown to be centered around the formation of thiomolybdates (mono-, di-, tri- and tetrathiomolybdates) in the rumen (27,28). Thiomolybdates are formed by molybdate reacting with sulfide. Sulfide is produced by rumen microorganisms via reduction of sulfate and also degradation of sulfur amino acids. Thiomolybdates associated with solid rumen digesta (bacteria, protozoa and undigested feed particles) form insoluble complexes with copper that do not release copper even under acidic conditions (29). Price et al. (30) found predominately tri- and tetrathiomolybdates in the solid phase of ruminal, duodenal and ileal digesta. Di- and trithiomolybdates were detected in the plasma of sheep after ruminal administration of $^{99}$Mo-labeled molybdate (30,31) and indicate that certain thiomolybdate species can be absorbed. Systemic effects on copper metabolism that were attributed to absorption of thiomolybdates include 1) increased biliary excretion of copper from liver stores; 2) strong binding of copper to plasma albumin, which results in reduced transport of available copper for biochemical processes; and 3) removal of copper from metalloenzymes (28).

When ruminal sulfide concentrations are low, molybdenum may have little effect on copper bioavailability. In sheep fed diets that contained only 1.0 g of sulfur/kg of diet, increasing the dietary molybdenum from 0.5 to 4.5 mg of molybdenum/kg of diet did not affect copper bioavailability (32). However, the addition of 3.0 g of sulfur and 4.0 mg of molybdenum/kg of diet to a basal diet that contained 1.0 g of sulfur and 0.5 mg of molybdenum/kg of diet reduced copper availability by 40–70% (32). With moderately high concentrations (2.7 g of sulfur/kg of diet) of sulfur in the diet, increasing dietary molybdenum from 5 to 10 mg of molybdenum/kg of diet did not further reduce copper status during a 196-d study with steers (33). This suggests that the synthesis of thiomolybdates may plateau with relatively low concentrations of molybdenum.

Independent from its role in the molybdenum-copper interaction, sulfur reduces copper bioavailability. Increasing dietary sulfur in the inorganic (sulfate) or organic (methionine) form from 1.0 to 4.0 g of sulfur/kg of diet reduced copper bioavailability in hypocupremic ewes fed low-molybdenum diets by 30–56% (34). Sulfur in the form of sulfide is believed to reduce copper bioavailability via formation of insoluble copper sulfide in the gut (34). Increasing dietary sulfur from 0.8 to 2.5 g of sulfur/kg of diet reduced omasal flow of soluble copper by ~50% in sheep (35). In this study, further increasing dietary sulfur to 4.4 g of sulfur/kg of diet had little additional effect on omasal flow of soluble copper.

**Iron.** Ruminants are often exposed to high iron intakes through ingestion of water, soil or feedstuffs that are high in iron. A number of studies indicate that addition of 250–1,200 mg of iron (from ferrous carbonate)/kg of diet greatly reduces copper status in cattle (36,37) and sheep (38). High dietary iron did not affect copper status in young preruminant calves, which suggests that a functional rumen is needed for iron to interfere with copper metabolism (36). It is unclear whether the antagonistic effects of iron and molybdenum on copper are additive (36).

**Supplemental sources of copper.** Cupric sulfate is the standard source to which other copper sources are compared. Copper from feed-grade copper oxide powder (primarily cupric oxide) is essentially unavailable in cattle. In calves that were deficient in copper, feeding of copper oxide did not increase plasma copper or ceruloplasmin activity relative to noncopper-supplemented calves (39). Copper oxide also was ineffective in preventing a decline in copper status when steers were fed a diet high in molybdenum and sulfur (39). Copper oxide needles were shown to supply available copper when administered orally to ruminants, and the needles were retained in the digestive tract and released copper for several weeks (24). Differences in copper availability between copper oxide powder
and needles can be explained by the much faster rate of passage of the powder compared to the needles. Copper oxide is relatively insoluble even under acidic conditions, and apparently the powder passes through the acidic environment in the abomasum before much, if any, copper can be solubilized. The relative bioavailability of copper from tribasic cupric chloride (Cu₂O·H₂O·Cl) was 121% (based on plasma copper) to 196% (based on liver copper) that of cupric sulfate when supplemented to cattle diets high in molybdenum and sulfur (40). The higher bioavailability of copper from tribasic copper chloride may relate to the low solubility of copper chloride in the rumen environment, which may reduce the potential for copper to interact with molybdenum and sulfur in the rumen. Tribasic copper chloride and cupric sulfate were similar in bioavailability when evaluated in copper-deficient steers fed diets that were low in molybdenum (40).

A number of studies evaluated various organic forms of copper. In cattle fed diets that were high in molybdenum, copper proteinate was more bioavailable than cupric sulfate in some studies (41,42) but not in others (43). Relative bioavailability of copper from copper lysine was generally similar to cupric sulfate (39,44). However, after stress (which was induced by feed and water restriction and adrenocorticotropic hormone administration), the apparent absorption and retention of copper were higher in steers fed copper lysine compared with those given cupric sulfate (45).

Zinc

The percentage of dietary zinc that is absorbed decreases as dietary zinc increases in ruminants (46). Zinc requirements of ruminants appear to be affected by dietary factors based on the variable animal responses that were observed after zinc supplementation (47). However, dietary factors that affect zinc bioavailability in ruminants are not clearly defined. Phytate can be degraded by microbial phytase in the rumen, and addition of phytate to diets of lambs with functional rumens did not reduce zinc status (48). High dietary calcium reduced serum zinc concentrations in ruminants (49,50), but elevated dietary calcium did not increase zinc requirements in lambs (50,51). A relatively large portion of zinc in forages is associated with the plant cell wall (1), but it is not known whether the association of zinc with fiber reduces absorption.

Supplemental sources of zinc. Studies in lambs indicate that zinc sulfate and zinc oxide are similar in bioavailability (52,53). Although the mode of action is unclear, research suggests that supplementing certain organic forms of zinc can improve animal-production responses (growth, milk production and/or reproduction) compared with those observed in ruminants that are supplemented with only inorganic zinc (54). Apparent absorption of zinc from zinc methionine and zinc oxide was similar when fed to zinc-deficient lambs (55). However, urinary excretion of zinc tended to be lower in lambs fed zinc methionine, which resulted in higher zinc retention. Zinc absorption from some organic zinc sources appears to be higher than from inorganic zinc when supplemented at high concentrations. Lambs supplemented with 360 mg of zinc/kg of diet from zinc lysine had much higher zinc concentrations in kidney, liver and pancreas than lambs that received zinc sulfate, zinc oxide or zinc methionine (56). Liver and plasma zinc concentrations were also higher in calves that were supplemented with 300 mg of zinc/kg of diet from a combination of zinc lysine and zinc methionine than in calves supplemented with zinc oxide (57). Higher tissue concentrations of zinc were also seen in calves (58) and lambs (59) that were fed high concentrations of zinc proteinate relative to the zinc concentrations observed in animals supplemented with zinc sulfate.

Manganese

Manganese is poorly absorbed (1% or less) from ruminant diets (60,61). Dietary factors that may influence manganese bioavailability have received little attention, probably because manganese deficiency is not considered to be a major problem in ruminants. Limited evidence suggests that high dietary calcium and phosphorus may reduce manganese bioavailability (60).

Manganese from two feed-grade manganese oxide sources tested in lambs was 70 and 53% as bioavailable as manganese from reagent-grade manganese sulfate (62). Relative bioavailability of manganese from manganese methionine was 120% of that present in the sulfate form (62).

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