

MÖSSBAUER SPECTROSCOPIC EVIDENCE FOR CITRATE-BICARBONATE-DITHIONITE EXTRACTION OF MAGHEMITE FROM SOILS

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Abstract—In a previous paper, we used powder X-ray diffraction and changes in magnetic susceptibility to argue the importance of pedogenic maghemite to soils and the efficacy of the chemical extractant citrate-bicarbonate-dithionite (CBD) to preferentially remove pedogenic maghemite from soil samples while not removing coarse-grained magnetite. Although X-ray diffraction provides strong support for this contention, Mössbauer spectroscopy is the method of choice for determining the oxidation state of iron in minerals and for inferring mineralogy of the iron oxide phases. Our objective in this work was to seek confirming evidence of the importance of maghemite as a pedogenic mineral and the usefulness of the CBD procedure in separating pedogenic maghemite from lithogenic magnetite. We present Mössbauer data on magnetic fractions from pre- and post-CBD treated soil samples. Six of the 10 samples had only maghemite as the sextet component and after CBD treatment, four lost between 96 and 100% of the magnetic susceptibility. Two samples were interpreted as highly oxidized magnetite or a mixture of magnetite and maghemite. We cannot distinguish between these with Mössbauer spectroscopy. In the remaining two samples, iron existed as hematite, ilmenite, magnetite and minor (<10%) amounts of maghemite. Our results provide additional support for pedogenic maghemite in soils and for the preferential removal of maghemite by the CBD procedure.

Key Words—Mössbauer spectroscopy, Soil genesis.

INTRODUCTION

Mineral magnetic parameters provide a quantitative means of studying the paleoclimate record of soils (Singer and Fine 1989, Fine *et al* 1989, Singer *et al* 1992). The magnetic susceptibility record of the vast loess deposits and associated paleosols of the Chinese loess plateau, for example, has provided a 2.4 million year history of continental climate change (Heller and Liu 1984, Kukla *et al* 1988, Liu *et al* 1992, Verosub *et al* 1993). A major issue in the interpretation of any mineral magnetic record from a soil is the mineralogy of the ferrimagnetic grains (Oldfield 1991). Le Borgne (1955) was the first to note the higher magnetic susceptibility of soil surfaces compared to parent material. He determined that the magnetic component of the clay layer (Bt horizon), which was the most magnetic, was maghemite and that it formed as a result of the alternate wetting and drying that is part of normal pedogenesis. Le Borgne also concluded that the high susceptibility was restricted to the humus-bearing layer because he believed that organic matter fermentation was responsible for producing the minerals carrying the magnetic susceptibility.

In a subsequent review, Mullins (1977) equivocated somewhat but seemed to agree with Le Borgne by using

the term pedogenic maghemite. However, Maher and Taylor (1988) and Schwertmann (1988) challenged the role of maghemite and suggested that the important mineral was magnetite. Our own results (Singer and Fine 1989, Singer *et al* 1992, Verosub *et al* 1993) agreed with those of Le Borgne and implied that maghemite can be a significant (but not necessarily the sole) contributor to the magnetic susceptibility signal in soils. We suggested that *in-situ* pedogenesis, Le Borgne's "born-on-the-spot" process, was responsible for the patterns of enhancement seen in many profiles around California (Singer and Fine 1989, Singer *et al* 1992).

Longworth *et al* (1979) concluded that secondary ferrimagnetic oxides in soil and bedrock may occupy a range of positions close to the solid solution series between stoichiometric magnetite and maghemite. In that work, both rock magnetic measurements and Mössbauer spectra were used to identify the iron oxides. In 1989, Fine and Singer (1989) showed that for a range of soil samples, the citrate-bicarbonate-dithionite (CBD) method preferentially removed pedogenic maghemite but left lithogenic magnetite unaffected. Fine and Singer based their conclusions about the presence of maghemite and magnetite on the interpretation of X-ray diffraction patterns. The objec-

Table 1. Characteristics of samples from which the magnetic fraction was removed for Mössbauer analysis, and magnetic susceptibility of the magnetic fraction.

Sample ID	Sample location/description	Soil horizon	Sample depth (cm)	Pre-CBD susceptibility (SI units)	Susceptibility loss after CBD (%)
1	Concretions from Mendocino, 112 m terrace	E	0–15	15,377	96
2	Concretions from Mendocino, 168 m terrace	Ec	0–18	15,808	79
3	Sacramento Valley Laguna formation	C	>1200	18,194	12
4	Concretions from Laguna formation	Bt1	46–71	16,541	23
5	Santa Cruz, beach sand	C	0–10	22,258	19
6	Santa Cruz 130 m terrace combination of 3 horizons	AB, 2Bt1, 2Bt2	23–190	21,612	63
7	Concretions from sample 6	AB, 2Bt1, 2Bt2	23–190	11,553	97
8	<2 μm fraction of sample 6	AB, 2Bt1, 2Bt2	23–190	not measured	
9	>0.25 mm concretions from Santa Cruz 130 m terrace, combination of 2 horizons	2Bt1, 2Bt2	60–190	7908	97
10	Santa Cruz, 220 m terrace; 0.25–1 mm concretions*	E	16–24	15,926	100

* Post-CBD analysis was completed on a whole soil sample, not just concretions. SI units are $10^{-8} \text{ m}^3 \text{ kg}^{-1}$.

tive of this paper is to offer Mössbauer spectra as supporting evidence for the usefulness of CBD extraction in differentiating between pedogenic maghemite and lithogenic magnetite.

MATERIALS AND METHODS

For the present study, we used soils that are representative of the range of magnetic mineralogies we have found in previous work (Table 1). For each soil, we removed the magnetic fraction from soil samples and concretions using both dry and slurry extraction with a hand magnet. The dry extraction was done by moving a hand magnet slowly through a small crucible into which the soil sample had been placed. Magnetic material clinging to the magnet was removed onto a glass plate which was placed on a magnetic stirrer. With the magnetic stirrer on, magnetic particles could be further segregated from non-magnetic particles. In the slurry procedure, a fine grade of steel wool was loosely packed in a glass column and hand magnets were taped to the outside of the column. A slurry of soil was cycled through the column at which time the magnetic material was attracted to the steel wool. After removing the magnets from the column, magnetic material was washed from the steel wool with distilled water and dried at 40°C.

The magnetic fraction was ground with a mortar and pestle to pass a 177 μm (80 mesh) sieve prior to chemical extraction and Mössbauer spectroscopy. Magnetic susceptibility was measured on samples prior to grinding by standard methods on a Bartington Model MS2 dual frequency (0.47 and 4.7 kHz) susceptibility meter equipped with a 36-mm-bore-diameter, Model MS2B sensor.

The CBD extraction procedure was developed for removing pedogenic iron oxides from clays (Mehra and Jackson 1960). Each magnetic fraction was extracted

twice with 2 g of sodium dithionite in hot (75°C) sodium citrate, sodium bicarbonate solution. After each extraction and centrifugation, the supernatant was decanted and the residual rinsed in cold sodium citrate, sodium bicarbonate solution. The residual material after two extractions and two rinses was dried at 40°C and gently crushed before Mössbauer spectroscopy.

We used a rhodium (Co-57) source of about 20 mCi to obtain room temperature Mössbauer spectra of both pre- and post-CBD treated samples. The constant acceleration Mössbauer spectrometer (Austin Science Associates, Austin, TX) was calibrated with a He-Ne laser interferometer. All spectra were fitted by a combination of sextets and doublets with Lorentzian line shape. Some of the pre-CBD samples (Table 2) required a distribution of magnetic fields to fit the asymmetric sextets (Amarasiriwardena *et al* 1986). In these cases, we report both the average field, B_{av} , and the field of maximum probability, B_{max} . The larger the difference between these two parameters, the more asymmetric the sextet.

Some samples were examined before and after CBD with a scanning electron microscope (Hitachi Scientific Instruments, Mountain View, CA) equipped with a Tracor Northern energy dispersive X-ray analyzer (Tracor Northern, Middleton, WI). Backscattered electron images were helpful in distinguishing among Fe-rich grains which appeared as bright images with strong backscatter signals and other minerals which were much darker. The EDAX analysis enabled us to further distinguish between purely Fe-rich and Fe plus Ti-rich magnetic grains.

RESULTS

Pre-CBD

The Mössbauer spectra of six of the ten samples (1, 2, 7, 8, 9, 10) had only maghemite (see Murad and

Johnston 1987, for literature values of parameters) as the sextet component (Figure 1; Table 2). After CBD treatment, four of these samples lost between 96 and 100% of their magnetic susceptibility. Thus the Mössbauer spectra support the interpretation made previously from the CBD extraction (Fine and Singer 1989) that in these cases, the mineral primarily contributing to the magnetic susceptibility was maghemite. All six of these samples had some Fe³⁺ doublet, and all required a distribution fit for the magnetic fields. The doublet is probably a silicate mineral phase; it is unlikely to be lepidocrocite because these soils are well-drained. The distribution of magnetic fields is characterized by large differences between the field of maximum probability, B_{max} , and the average field B_{av} . This result is probably due to the poor crystallinity of the maghemite.

The presence of maghemite in sample 8, which is the clay fraction of sample 6, supports our contention that pedogenic maghemite is a weathering product in soils; the unweathered parent material of this sample had no clay-sized maghemite, based on its resistance to CBD extraction.

Spectra from two samples (5 and 6) were interpreted as highly oxidized magnetite or a mixture of magnetite and maghemite. These two possibilities cannot be distinguished by Mössbauer spectroscopy. When we examined magnetic particles from these samples using back-scattered electron microscopy images, we found the bright grains are fractured, pitted and have rounded edges which we interpret as due to weathering (Figure 2). The elemental composition of these bright grains,

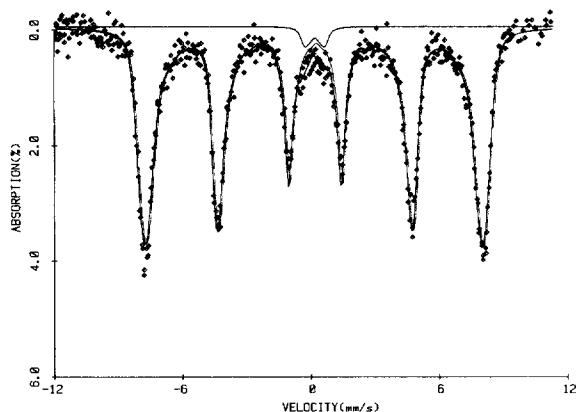


Figure 1. Mössbauer spectra of untreated (pre CBD) soil sample 1.

determined by EDAX, was Fe only or Fe and Ti. This favors the interpretation that highly oxidized magnetite or titanomagnetite is present in these samples.

If we assume the Mössbauer sextets (Table 2) are due to a mixture of magnetite ($1.5 \times$ relative area MO) and maghemite (relative area MT $-0.5 \times$ relative area MO), we can calculate the percentages of the two components. We find that for sample 5, 57% of the iron could exist as stoichiometric magnetite with 35% as maghemite. For sample 6, 27% of the iron could be magnetite with 63% as maghemite. An alternative interpretation is that both the sextets correspond to magnetite alone. In this case, sample 6 has 90% of the iron as magnetite, but the magnetite is highly oxidized, with

Table 2. Best fit data for Mössbauer spectra of untreated (Pre-CBD) magnetic fraction removed from soil samples.

Sample ID	Sextets						Doublets			
	IS/Fe	QS ¹ (mm/s)	B_{max}	B_{av} Tesla	RA ² (%)	Asm ³	IS/Fe	QS ¹ (mm/s)	RA ² (%)	Asm ³
1	0.34	-0.05	48.9	44.8	98	MG	0.3	0.8	2	Fe ³⁺ (G)
2	0.34	-0.05	49.2	44.6	97	MG	0.4	0.7	3	Fe ³⁺ (Si)
3	0.38	-0.15	51.3	—	27	H	0.25	0.54	2	Fe ³⁺ (Si)
	0.31	(0.0)	48.7	—	27	MT	1.08	0.67	5	Fe ²⁺ (I)
4	0.68	(0.0)	45.5	—	39	MO				
	(0.39)	(-0.20)	50.7	—	25	H	0.27	0.44	18	Fe ³⁺ (Si)
	(0.28)	(0.0)	48.0	—	11	MT	1.06	0.64	35	Fe ²⁺ (I)
	(0.66)	(0.0)	43.9	—	10	MO				
5	0.29	(0.0)	48.8	39.1	54	MT	0.16	0.4	2	Fe ³⁺ (Si)
	0.67		45.7	45.6	38	MO	1.15	0.88	5	Fe ²⁺ (I)
6	0.35	(0.0)	49.3	40.4	72	MT	0.18	0.52	4	Fe ³⁺ (Si)
	0.65		45.6	45.4	18	MO	1.10	0.70	6	Fe ²⁺ (I)
7	0.34	-0.03	49.0	43.3	88	MG	0.38	0.67	12	Fe ³⁺ (Si)
8	0.36	-0.11	49.4	40.4	37	MG	0.36	0.60	63	Fe ³⁺ (Si)
9	0.34	-0.03	48.2	40.1	76	MG	0.38	0.70	24	Fe ³⁺ (Si)
10	0.33	-0.02	48.5	40.9	84	MG	0.36	0.66	16	Fe ³⁺ (Si)

¹ Quantities in parentheses were fixed parameters. For distribution fits, both B_{max} and B_{av} are reported. The greater the difference between them, the more asymmetric the sextet distribution. If B_{av} is not reported, the sextet was not distributed, and $B_{max} = B_{av}$.

² Relative area.

³ Assignment: MG = maghemite, MT, MO = magnetite, H = hematite, I = ilmenite, Si = silicate, G = goethite.



Figure 2. Backscatter electron image from sample 6 after CBD treatment. Elemental composition of bright grains determined by EDAX is predominantly Fe and Ti.

only 10% of its iron as Fe^{2+} rather than the stoichiometric 33% of Fe_3O_4 . The relative contribution of Fe^{2+} is $\frac{1}{2}$ of the octahedral site occupancy labelled MO in Table 2, i.e., 9% vs 72% MT Fe^{3+} and 9% MO Fe^{3+} for sample 6. The ferrous doublet in these two samples has a relatively small average QS. We interpret this as due to ilmenite (FeTiO_3), by comparison with the literature (Murad and Johnston 1987).

In the remaining two samples (3 and 4), a portion of the iron exists as hematite (Figure 3). This phase is distinguishable by the characteristic field of 51 to 52T and the negative QS of about -0.2 mm/s (Murad and Johnston 1987). Sample 3 has magnetite as the major iron species with some ilmenite. The IS/Fe = 1.08 and QS = 0.67 mm/s of the ferrous doublet is characteristic of ilmenite. Sample 4 has much more ilmenite than sample 3, and its sextet component was difficult to fit

because of the weak intensity and broadened line width. If we again assume a mixture, then about 15% of the iron in this sample could exist as magnetite compared with 58% in sample 3. Both samples would then have essentially the same amount of maghemite; 6% in sample 4 and 8% in sample 3. As in samples 5 and 6, rather than maghemite plus magnetite, these samples could have oxidized magnetite alone, with sample 4 being more oxidized (24% Fe^{2+}) than sample 3 (30% Fe^{2+}).

Post-CBD

Mössbauer spectra were obtained for five samples (1, 3, 5, 6 and 10) from the original set after CBD extraction. All of the samples had magnetite as a major component as indicated by the presence of the two characteristic sextets labeled MT or MO in Table 3 and shown in Figure 4. In no case did we observe the

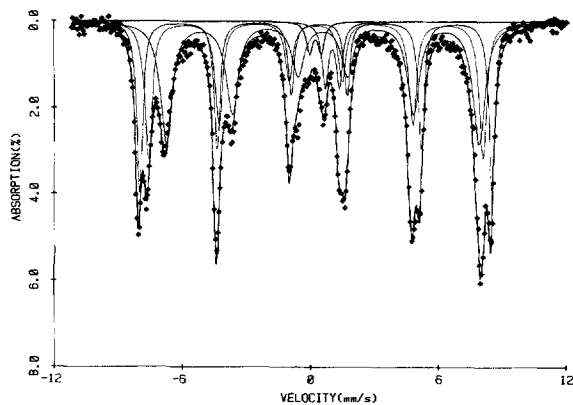


Figure 3. Mössbauer spectra of untreated (pre CBD) soil sample 3.

stoichiometric 2:1 ratio of octahedral (MO) to tetrahedral (MT) components, indicative of unweathered magnetite. Sample 1, with a ratio of 0.4:1, was the most highly oxidized. The closest value was for sample 10 which had a ratio of 2.5:1. However, the Mössbauer spectrum of this sample had very large line widths, making the relative area (RA) values uncertain to greater degree than for the other samples. The large width indicates that smaller magnetite particles are present in this sample. All samples except sample 1 had an Fe^{2+} component with low QS (0.6–0.7 mm/s) and high IS/Fe (1.05–1.08). It is likely that the component is ilmenite based on these parameters (Murad and Johnston 1987). Sample 3 was the only one that had a significant amount (15%) of hematite as a third component.

DISCUSSION

The present study supports our earlier work that found maghemite can be a major or even the sole fer-

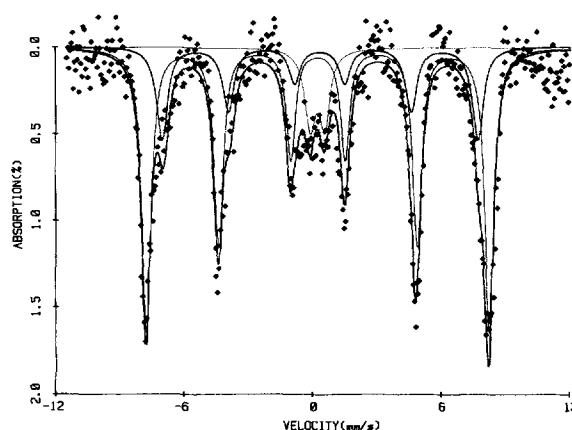


Figure 4. Mössbauer spectra of treated (post CBD) soil sample 1.

rimagnetic component in soils. In six of our samples (1, 2, 7, 8, 9, and 10), the pre-CBD Mössbauer spectra were consistent with the presence of only one ferri-magnetic component, namely, maghemite. In four of these samples (1, 7, 9, and 10), over 96% of the magnetic susceptibility signal disappeared after the CBD extraction, which leaves little doubt that the original magnetic susceptibility signal was due to maghemite.

In four of the other samples (3 through 6), the ferri-magnetic sextets could be interpreted as being due either to oxidized magnetite or to a mixture of magnetite and maghemite. These two interpretations are not mutually exclusive. One of the postulated mechanisms for the production of maghemite in soils is the oxidation of magnetite. Özdemir *et al* (1993) have recently shown that this process proceeds by the formation of a progressively thicker rind of maghemite around a magnetite core. Thus maghemite that is present in a soil whose parent material contains magnetite

Table 3. Best fit data for Mössbauer spectra of treated (post-CBD) magnetic fraction removed from soil samples

Sample ID	Sextets					Doublets			
	IS/Fe	QS ¹ (mm/s)	B Tesla	RA ² (%)	Asm ³	IS/Fe	QS ¹ (mm/s)	RA ² (%)	Asm ³
1	0.32	(0.0)	49.8	65	MT	0.31	0.68	9	Fe ³⁺ (Si)
	0.51	(0.0)	45.8	26	MO				
3	0.28	(0.0)	48.7	25	MT	0.27	0.54	6	Fe ³⁺ (Si)
	0.64	(0.0)	45.5	40	MO				
5	0.41	-0.2	51.0	15	H	1.05	2.80	2	Fe ²⁺ (Si)
	0.32	(0.0)	49.3	31	MT				
	0.66	(0.0)	45.8	22	MO				
6	0.30	(0.0)	48.9	40	MT	0.31	0.58	9	Fe ³⁺ (Si)
	0.65	(0.0)	45.4	37	MO				
	0.36	(0.0)	48.6	20	MT				
10	0.36	(0.0)	48.6	20	MT	0.24	0.42	10	Fe ³⁺ (Si)
	0.63	(0.0)	44.5	49	MO				
						1.07	0.70	21	Fe ²⁺ (I)

¹ Quantities in parentheses were fixed parameters.

² Relative area.

³ Assignment: MT, MO = magnetite, H = hematite, I = ilmenite, Si = silicate.

could occur as maghemite rinds on magnetite cores, as separate authigenic maghemite grains or as both. The maghemitized magnetite grains would appear under the scanning electron microscope as highly oxidized magnetite. Separately formed maghemite grains probably occur most frequently where the pedogenic enhancement of the magnetic susceptibility is quite large (Singer *et al* 1992, Verosub *et al* 1993).

Our results provide confirmation of the effects of the CBD extraction. In previous work (Singer and Fine 1989, Singer *et al* 1992), we suggested that the CBD extraction preferentially solubilized (pedogenic) maghemite with respect to (lithogenic) magnetite. The Mössbauer results presented here support our earlier statements. No maghemite was found in any of the six post-CBD Mössbauer spectra.

The sextets from the spectra for samples 1 and 10 prior to CBD extraction were interpreted as maghemite without magnetite. As noted in Table 1, the post-CBD Mössbauer spectrum for sample 10 was obtained from magnetic particles removed from all soil material > 50 μm diameter. The spectrum contained (lithogenic) magnetite in the matrix and an Fe^{2+} doublet probably due to ilmenite but no maghemite. This spectrum cannot be compared directly with the pre-CBD spectra of sample 10 which was obtained from magnetic material removed from concretions in the soil. However, concretions were included in material used for the post-CBD sample, and the absence of maghemite indicates that the CBD-extraction removed whatever maghemite was present in the concretions. The concretions are clearly pedogenic features. Thus these results support the conclusion that CBD selectively removes pedogenic maghemite.

The post-CBD spectrum for sample 1 indicates the presence of magnetite, but no magnetite was observed in the pre-CBD sample. The magnetic susceptibility of other subsamples from sample 1 was nearly zero after CBD treatment, indicating complete removal of maghemite and the absence of magnetite. We believe that the magnetite detected in the post-CBD sample was obscured in the pre-CBD sample by the large amount of maghemite in that sample. The magnetite was probably occluded in the maghemite, perhaps as the magnetite cores of maghemitized grains. Although all samples were ground to pass through a 177 μm hole sieve to reduce the problem of occlusion, apparently this procedure was insufficient for this sample. Sample 1 also contained a small amount (2%) of goethite before CBD treatment, but no goethite after CBD treatment. This result is consistent with other results of CBD extraction.

Prior to the CBD-extraction, the Mössbauer spectra of samples 3, 5 and 6 indicated substantial amounts of magnetite (Table 2). Based on relative areas for MT and MO, the magnetite was almost stoichiometric in sample 3 (30% Fe^{2+} vs 33% for Fe_3O_4), but either highly-oxidized or mixed with maghemite in sample 5

(21% Fe^{2+}) and sample 6 (10% Fe^{2+}). After CBD extraction (Table 3), sample 3 had essentially the same relative area and stoichiometry (31% Fe^{2+}) for its magnetite, while the relative area due to magnetite decreased markedly for the other two. However, the stoichiometry remained the same for sample 5 (21% Fe^{2+} after extraction) but became less oxidized for sample 6 (24% Fe^{2+}). These results indicate that stoichiometric magnetite (sample 3) is not extracted, while oxidized magnetite is to some extent (sample 5). The change in oxidation for sample 6 can only be explained by assuming the original magnetite was actually a mixture with maghemite, whose removal by extraction increased the relative area of MO compared to MT and thus the proportion of Fe^{2+} in the remaining magnetite.

Typically, CBD removes secondary hematite from soils, and it is surprising to us that hematite remained in sample 3 after CBD treatment. Two possible explanations are that the hematite was occluded within magnetite grains and was protected from the CBD, or that the hematite is sufficiently coarse-grained in this sample that it was not completely consumed by the CBD extraction. The sample was taken from a depth of more than 12 m in a deeply developed soil profile that may represent 1.6 million years of pedogenesis (Busacca 1982). The presence of coarse-grained hematite in the original sample would not be surprising.

Finally, we note that the relative amount of the doublet components (silicates, ilmenite) increased for samples 1, 3, 5 and 6, which is expected if maghemite is being removed by the CBD extraction. For samples 1 and 6, the magnetite proportion increased markedly after CBD treatment. Although the magnetite hardly changed for sample 3, some of the hematite was removed which increased the area of the doublets.

CONCLUSIONS

Our results from Mössbauer spectra collected from pre- and post-CBD extracted samples of magnetic material from soil samples confirm that maghemite is the dominant ferrimagnetic mineral in some soils and that CBD extraction is very effective in removing maghemite from soil samples. The CBD method, in conjunction with magnetic susceptibility and Mössbauer spectroscopic measurements made before and after the CBD extraction, represents an additional approach for studying the magnetic mineralogy of fine-grained sediments and soils.

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