Magnetic enhancement is linked to and precedes hematite formation in aerobic soil

José Torrent,[1] Vidal Barrón,[1] and Qingsong Liu[2]

Received 30 September 2005; revised 1 December 2005; accepted 6 December 2005; published 18 January 2006.

[1] Soil formation usually increases magnetic susceptibility, most often by increasing the concentrations of magnetite and maghemite, which are two ferrimagnetic iron oxides. Here we provide evidence that magnetic enhancement in aerobic soils not affected by detrital magnetic inputs or thermal transformation of other iron oxides is mostly due to the formation of maghemite, which is later transformed into hematite—the iron oxide that gives red color to soil. We show that the maghemite/hematite ratio is influenced by the particular environment and the degree of soil development, so it constitutes an effective tool for paleoenvironmental and planetary studies. **Citation:** Torrent, J., V. Barrón, and Q. Liu (2006), Magnetic enhancement is linked to and precedes hematite formation in aerobic soil, *Geophys. Res. Lett.*, *33*, L02401, doi:10.1029/2005GL024818.

1. Introduction

[2] Soil formation usually increases magnetic susceptibility, most often by increasing the concentrations of ferrimagnetic minerals [*Tite and Linington*, 1975; *Evans and Heller*, 2003]. In soils not affected by detrital magnetic inputs, waterlogging, and/or thermal transformations of other iron (hydr)oxides, magnetic enhancement is ascribed to the neoformation of nanosized magnetite and/or maghemite [*Dearing et al.*, 1996a]. Both inorganic [*Maher and Taylor*, 1988] and bacterially mediated [*Fassbinder et al.*, 1993; *Lovley et al.*, 1987] pathways to magnetite have been proposed that require the presence of reductive conditions and the resulting accumulation of Fe^{2+} in the soil solution. However, this assumption is challenged by the coexistence of pedogenic ferrimagnets and hematite in soils [*Balsam et al.*, 2004] because hematite rarely forms in significant amounts in soil environments undergoing Fe reduction [*Schwertmann*, 1985]. Here we test the hypothesis that maghemite and hematite form paragenetically in aerobic soils. This hypothesis is supported by (i) the in vitro ferrihydrite→ maghemite → hematite transformation that is observed for ferrihydrite doped with phosphate or the anions of some low molecular weight organic acids [*Barrón and Torrent*, 2002], and (ii) the fact that any pedogenic magnetic enhancement in aerobic soils containing no pedogenic hematite is limited, as discussed later on.

[1] Departamento de Ciencias y Recursos Agrícolas y Forestales, Universidad de Córdoba, Córdoba, Spain.
[2] School of Ocean and Earth Science, Southampton Oceanography Centre, Southampton, UK.

0094-8276/06/2005GL024818$05.00

2. Materials and Methods

[3] To determine the relationships between the magnetic enhancement and hematite content in soils, we characterised samples from soils and paleosols in world regions where present or past climatic conditions are believed to have favoured neoformation of hematite [*Schwertmann*, 1985]. Upper A horizons were excluded from study in order to avoid the potential effects of contamination with aerial magnetic inputs and maghemite resulting from the thermal transformation (by fire) of other Fe oxides. The samples we analyzed were provided by different authors. The origin and basic characteristics of these samples are reported in the references given in the captions of Figures 1 to 3.

[4] The samples were ground to <2 mm and analyzed for total Fe (Fe_t) (HF − $HClO_4$ digestion), citrate/bicarbonate/dithionite(CBD)-extractable Fe (Fe_d) and acid oxalate-extractable Fe (Fe_o) by standard methods [*Cornell and Schwertmann*, 2003]. We used Fe_d as a measure of the Fe content in Fe oxides and the Fe_d/Fe_t ratio as one of the degree of weathering of Fe-bearing minerals to secondary Fe oxides. We quantitatively estimated the contents of hematite and goethite in soil from the visible spectra of pressed fine powders, which were recorded on a Cary 1E spectrophotometer equipped with a diffuse reflectance ac-

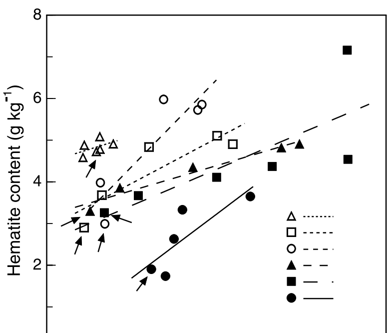

Figure 1. Relationship between hematite content and frequency-dependent magnetic susceptibility (χ_{FD}) in soil profiles developed on loess of the Russian steppe [*Maher et al.*, 2002] in areas with mean annual precipitation (MAP) of 300 mm (open triangles), 340 mm (open circles), 380 mm (open squares), 450 mm (solid triangles) and 480 mm (solid squares) and on Argentinian Pampa loess with MAP of 1000 mm (GAO soil) [*Nabel et al.*, 1999] (solid circles). The regression line and the parent loess (arrow) for each profile are shown. In all profiles, smooth changes in the Fe_d/Fe_t ratio indicated that the parent loess was essentially homogeneous.

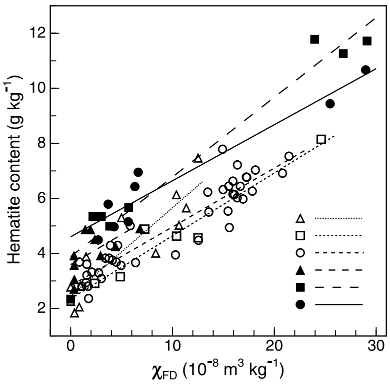

Figure 2. Relationship between hematite content and χ_{FD} in loess/paleosol profiles from different sections of the Chinese Loess Plateau: Yuanbao [*Liu et al.*, 2004] (open triangles), Luochuan [*Balsam et al.*, 2004] (open squares), Yichuan [*Liu et al.*, 2004] (open circles), Huanxian [*Ji et al.*, 2004] (solid triangles), Lingtai L4/S3 (solid squares), and Lingtai L6/S5 [*Spassov et al.*, 2003] (solid circles). The regression line is shown for each profile, which comprises a paleosol and the overlying and/or underlying loess. In all profiles, smooth changes in the Fe_d/Fe_t ratio indicated that the parent loess was essentially homogeneous.

cessory. The bands of the second derivative of the Kubelka–Munk function spectrum were used for this purpose [*Scheinost et al.*, 1998]. Mass specific magnetic susceptibility (χ) at low (465 Hz, χ_{LF}) and high (4650 Hz, χ_{HF}) frequencies was measured with a Bartington Instrument Ltd MS2B Dual Frequency Sensor.

[5] Here we used the frequency-dependent magnetic susceptibility ($\chi_{FD} = \chi_{LF} - \chi_{HF}$) as a semiquantitative measure of the concentration of pedogenic fine-grained magnetic grains. This choice is strongly supported by the high correlation we found between χ_{FD} and the loss of χ upon application of the CBD treatment [CBD-extractable $\chi = 22 + 6.2\ \chi_{FD}$ (10^{-8} m^3 kg^{-1}); $R^2 = 0.99$; $P < 0.001$; $n = 128$)] as CBD can efficiently dissolve pedogenic magnetite/maghemite but not aeolian (detrital) magnetite grains [*Vidic et al.*, 2000]. To estimate the concentration of pedogenic magnetite/maghemite in soil we assumed (i) $\sim 800 \times 10^{-6}$ m^3 kg^{-1} to be a typical value of χ for superparamagnetic magnetite/maghemite, as reported by *Maher* [1988], and (ii) $\sim$12% to be the relative frequency-dependent χ value (i.e., χ_{FD}/χ_{LF}) of this magnetite/maghemite, as suggested by the work of *Dearing et al.* [1996b]. Then, the mass fraction of pedogenic magnetite/maghemite (i.e., mass of magnetite/maghemite per unit soil mass) is given by the expression: $(\chi_{FD}/0.12)/(800 \times 10^{-6}$ m^3 kg$^{-1})$.

3. Results

[6] We present various types of hematite-χ_{FD} relationship in soils. Figure 1 shows such a relationship for six Holocene soil profiles developed on loess that generally contained little hematite (five in the Russian steppe and one in the Argentinian Pampa). Positive, significant ($P < 0.10$) correlations between these variables were observed in all soils except one from an area with mean annual precipitation (MAP) of $\sim$300 mm, which exhibited little weathering (its Fe_d/Fe_t was constant throughout the studied profile). The slope of the hematite$-\chi_{FD}$ regression line for the Russian soils was smaller for the soils from areas with the higher rainfall. The average slope of the regression lines in Figure 1 is $\sim$0.4 g hematite kg^{-1}/10^{-8} m^3 kg^{-1}. This value is equivalent to a mass ratio between hematite and magnetite/maghemite of $\sim$4.

[7] Figure 2 shows similar plots for six loess/paleosols profiles from five different locations in the Chinese Loess Plateau (CLP). The slopes of the regression lines differ little from those for the Russian steppe soils, suggesting that the pedogenic pathways in these two adjacent regions are identical. The greatest slope corresponds to the Yuanbao paleosol, collected in an area with a current MAP that is low relative to the other areas (500 vs. >600 mm); on the other hand, the smallest slope is that for one of the Lingtai loess/paleosols profiles, in an area with a current MAP of 650 mm.

[8] The soils/paleosols shown in Figures 1 and 2 were formed in cold temperate to temperate climates; accordingly, they exhibit scarce weathering. Thus, Fe_d/Fe_t increases little from the parent loess to the most heavily weathered soil

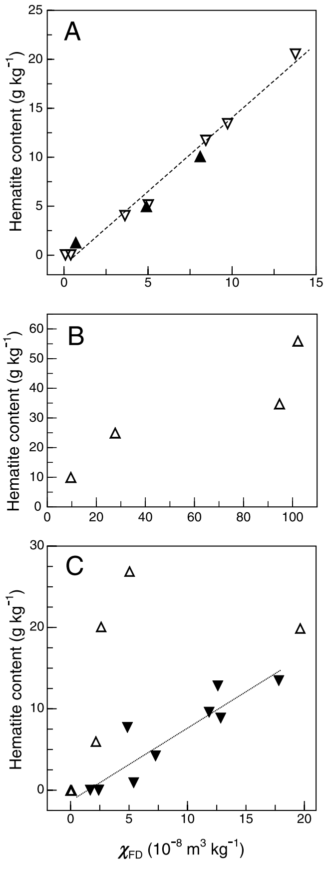

Figure 3. Relationship between hematite content and χ_{FD} in soils of Mediterranean regions. (a) A reddish brown soil profile on calcarenite in Spain [*Torrent and Cabedo*, 1986] (open triangles and regression line) and a reddish brown paleosol on loess in Moravia [*van Oorschot et al.*, 2002] (solid triangles). (b) Horizons of Terra Rossa developed on limestone or dolomite residuum from Italy, Portugal and USA. (c) Horizons of soils on a river terrace sequence in northern Spain [*Torrent*, 1976] (solid triangles, regression line) and in southern Spain [*Peña and Torrent*, 1984; *Duiker et al.*, 2003].

horizons (from ~0.25 to <0.33 in the Russian soils, 0.06 to 0.18 in the Argentinian soil, and ~0.23 to 0.37 in the CLP paleosols). The amount of neoformed hematite is therefore quite modest (<10 g kg^{-1} soil) and so is that of neoformed goethite. Higher concentrations of hematite are found in soils from areas with warm temperate to hot, subhumid to humid climates, provided the soils are well-drained, poor in organic matter, and subject to seasonal drying. These conditions favour dehydration of precursor ferrihydrite to hematite rather than dissolution of ferrihydrite and nucleation of goethite [*Schwertmann*, 1985].

[9] Figure 3 shows the hematite contents and χ_{FD} values for the Mediterranean soils, where rubefaction (*viz.* reddening due to pedogenic hematite) is quite commonplace. In a rubefacted soil profile (Figure 3a) formed on a homogeneous hematite-free calcarenite exhibiting negligible χ_{FD} (<2 × 10^{-8} m^3 kg^{-1}), the maximum concentration of hematite (>20 g kg^{-1}) is substantially higher than that of the Russian and CLP soils and so is the slope of the hematite–χ_{FD} regression line (1.51 g hematite $kg^{-1}/10^{-8}$ m^3 kg^{-1}, equivalent to a hematite to magnetite/maghemite ratio of ~15). Typical Terra Rossas developed on limestone residuum exhibit high (>10 g kg^{-1}) hematite contents and variable hematite/χ_{FD} ratios (Figure 3b). The B horizons of Alfisols developed on river terrace materials in two areas of Spain (Figure 3c) also illustrate the paragenesis of hematite and magnetite/maghemite in Mediterranean areas. Similarly, highly weathered soils from tropical and subtropical areas tend to exhibit significant pedogenic magnetic enhancement only when they contain pedogenic hematite, irrespective of their, sometimes high, content in goethite. For instance, in the B horizons of three Oxisols of the Brazilian cerrado region that were similar in properties except for the type of Fe oxide, χ_{FD} was 62 × 10^{-8} m^3 kg^{-1} for the one rich in hematite, 21 × 10^{-8} m^3 kg^{-1} for the one that contained more goethite than hematite, and only 2 × 10^{-8} m^3 kg^{-1} for the one that contained goethite but not hematite (J. Torrent, unpublished results).

4. Discussion

[10] The soil hematite–magnetite/maghemite paragenesis is consistent with the ferrihydrite $\xrightarrow{1}$ superparamagnetic (SP) maghemite $\xrightarrow{2}$ single domain (SD) maghemite $\xrightarrow{3}$ hematite transformation. This has previously been observed for synthetic 2-line ferrihydrite doped with phosphate or citrate and aged at >150°C [*Barrón and Torrent*, 2002; Q. S. Liu et al., Magnetism of the intermediate maghemite in the transformation of 2-line ferrihydrite into hematite and its paleoenvironmental implications, submitted to *Earth and Planetary Science Letters,* 2005]. Based on our model, various ligands present in the soil solution are sorbed on the surface of ferrihydrite particles, which are thus "blocked" and can undergo internal rearrangement and slow dehydration to hematite via steps 1 and 2. Experiments underway (V. Barrón) have shown that ferrihydrite becomes hematite at 25°C at a rate that is dictated by content in doping ligands; however, the transformation always involves a transient, significant increase in χ.

[11] Our model postulates the direct formation of a phase that exhibits most of the characteristics of maghemite rather than magnetite. This is supported by the fact that samples of various Mediterranean soils and paleosols from the CLP exhibited a decrease in χ_{FD} upon oxalate extraction that was less than 40% of the result obtained by CBD extraction. We observed that this maghemite is resistant to oxalate extraction in contrast to magnetite in the submicron size range, which is quantitatively dissolved as a result of the well-known Fe^{2+}–induced autocatalytic effect [*Reyes and Torrent*, 1997].

[12] Many observations indicate that little or no hematite —and, based on our model, maghemite— is formed when the soil environmental conditions favour dissolution of ferrihydrite (whether by reduction, acidification or complexation with organic matter). Then, the hydrolysis of Fe ions in solution results in the formation of goethite or —less frequently— lepidocrocite [*Schwertmann*, 1985]. The fact that goethitic (i.e., hematite-free, but goethite-containing) soils exhibit limited substantial magnetic enhancement contradicts currently prevailing hypotheses that ascribe the enhancement mostly to the inorganic or biotic synthesis of magnetite [*Dearing et al.*, 1996a]. This process requires the presence of Fe^{2+} in solution, a condition that is met in soil horizons and environments that are water saturated, and hence undergo reduction, in some periods. This moisture regime is likely to favour the transformation of ferrihydrite (via dissolution) into goethite rather than hematite. A typical example is provided by the river terrace soils of Figure 3c, which contain 10–60 g goethite kg^{-1}: the goethitic, χ_{FD}–poor soils exhibit some field properties suggesting somewhat imperfect drainage in winter, whereas their hematitic counterparts do not [*Peña and Torrent*, 1984; *Torrent*, 1976]. If these hypotheses were fulfilled on a significantly large scale, then one could expect magnetic enhancement in goethitic soils to exceed that in similar hematitic soils, which is obviously not the case. Indeed, magnetite formation to significant extent in anaerobic microenvironments in otherwise well-drained soils cannot be excluded [*Maher and Taylor*, 1988].

[13] A long-sustained, alternative explanation for the strong link between hematite formation and magnetic enhancement in soil undergoing wet/dry cycles (e.g., Mediterranean soils) is reductive dissolution of hematite/goethite in the wet season followed by magnetite formation and then oxidation to maghemite in the dry season [*Maher*, 1998]. This however clashes with the fact that maghemite is more soluble than either hematite or goethite [*Cornell and Schwertmann*, 2003], and thus likely to be redissolved with the onset of wet conditions after the dry season. Moreover, the positive correlation between hematite and maghemite concentrations in our studied soil profiles does not support a genetic transformation of hematite to magnetite through reduction and then to maghemite through reoxidation.

[14] Our results indicate that the soil hematite/χ_{FD} ratio relates, among other factors, to pedoclimate and the degree of weathering. Such factors are likely to influence the rates of ferrihydrite formation from weatherable Fe-bearing minerals and steps 1 to 3 of the proposed pathway in a predictable way. In soils remaining moist, but not saturated most of the year, and warm enough for significant mineral transformation, the rates of ferrihydrite formation, and of steps 1 and 2, are likely to be relatively fast compared to step 3, which involves both ion rearrangement and dehydration. By contrast, soils in areas with lower rainfall and

longer dry seasons are likely to exhibit a faster step 3 and higher hematite/χ_{FD} ratios than the previous ones. Thus, as noted earlier, the hematite/χ_{FD} ratio tends to increase with decreasing rainfall in the Russian steppe soils (Figure 1) and CLP paleosols (Figure 2), consistent with previous findings [*Balsam et al.*, 2004]. Similarly, in tropical regions, Oxisols undergoing seasonal drying tend to exhibit higher hematite/χ_{FD} ratios than those that do not. So, J. Torrent (unpublished results) found this ratio to be >2 g hematite $kg^{-1}/10^{-8}$ m^3 kg^{-1} for a group of Brazilian Oxisols subjected to a dry season (Ustoxs), but only <1 g hematite $kg^{-1}/10^{-8}$ m^3 kg^{-1} for another group of Brazilian Oxisols that were moist for most of the year (Udoxs). It must also be noted that highly weathered hematitic soils are likely to be poor in χ_{FD} relative to other soils as the intermediate products formed in the conversion of Fe-bearing minerals to hematite are gradually depleted. Hence the potential use of our findings for characterizing soil formation environments. This applies not only to terrestrial soils and paleosols, but also to the Fe oxide-rich Martian soils and dusts [*Barrón and Torrent*, 2002].

[15] **Acknowledgments.** We thank T. Alekseeva, W. Balsam, M. J. Dekkers, F. Heller, J. F. Ji, H. Morrás and F. E. Rhoton for providing samples, A. Alekseev for magnetic characterization of some samples, and B. Maher for discussions. This work was supported by the Spain's Ministerio de Ciencia y Tecnología, Project AGL2003–01510.

References

Balsam, W., J. F. Ji, and J. Chen (2004), Climatic interpretation of the Luochoan and Lingtai loess sections, China, based on changing iron oxide mineralogy and magnetic susceptibility, *Earth Planet. Sci. Lett.*, *223*, 335–348.

Barrón, V., and J. Torrent (2002), Evidence for a simple pathway to maghemite in Earth and Mars soils, *Geochim. Cosmochim. Acta*, *66*, 2801–2806.

Cornell, R. M., and U. Schwertmann (2003), *The Iron Oxides*, 2nd ed., 664 pp., John Wiley, New York.

Dearing, J. A., K. L. Hay, S. M. J. Baban, A. S. Huddleston, E. M. H. Wellington, and P. J. Loveland (1996a), Magnetic susceptibility of soil: An evaluation of conflicting theories using a national data set, *Geophys. J. Int.*, *127*, 728–734.

Dearing, J. A., R. J. L. Dan, K. Hay, J. A. Lees, P. J. Loveland, B. A. Maher, and K. O'Grady (1996b), Frequency-dependent susceptibility measurements of environmental materials, *Geophys. J. Int.*, *124*, 228–240.

Duiker, S. W., F. E. Rhoton, J. Torrent, N. E. Smeck, and R. Lal (2003), Iron (hydr)oxide crystallinity effects on soil aggregation, *Soil Sci. Soc. Am. J.*, *67*, 606–611.

Evans, M. E., and F. Heller (2003), *Environmental Magnetism*, 299 pp., Elsevier, New York.

Fassbinder, J. W. E., H. Stanjek, and H. Vali (1993), Occurrence of magnetic bacteria in soil, *Nature*, *343*, 161–163.

Ji, J. F., W. Balsam, H. Y. Lu, Y. B. Sun, and H. F. Xu (2004), High resolution hematite/goethite records from Chinese loess sequences for the last glacial-interglacial cycle: Rapid climatic response of the East Asian Monsoon to the tropical Pacific, *Geophys. Res. Lett.*, *31*, L03207, doi:10.1029/2003GL018975.

Liu, Q., S. K. Banerjee, M. J. Jackson, B. A. Maher, Y. Pan, R. Zhu, C. Deng, and F. Chen (2004), Grain sizes of susceptibility and anhysteretic remanent magnetization carriers in Chinese loess/paleosol sequences, *J. Geophys. Res.*, *109*, B03101, doi:10.1029/2003JB002747.

Lovley, D. R., J. F. Stolz, J. L. Nord, and E. J. P. Phillips (1987), Anaerobic production of magnetite by a dissimilatory iron-reducing microorganism, *Nature*, *330*, 252–254.

Maher, B. A. (1988), Magnetic properties of some synthetic submicron magnetites, *Geophys. J.*, *94*, 83–96.

Maher, B. A. (1998), Magnetic properties of modern soils and Quaternary loessic paleosols: Paleoclimatic implications, *Palaeogr. Palaeocl. Palaeoecol.*, *137*, 25–54.

Maher, B. A., and R. M. Taylor (1988), Formation of ultrafine magnetite in soils, *Nature*, *336*, 368–370.

Maher, B. A., A. Alekseev, and T. Alekseeva (2002), Variation of soil magnetism across the Russian steppe: Its significance for use of soil magnetism as a palaeorainfall proxy, *Quat. Sci. Rev.*, *21*, 1571–1576.

Nabel, P. E., H. J. M. Morrás, N. Petersen, and W. Zech (1999), Correlation of magnetic and lithologic features of soils and Quaternary sediments from the Undulating Pampa, Argentina, *J. S. Am. Earth Sci.*, *12*, 311–323.

Peña, F., and J. Torrent (1984), Relationships between phosphate sorption and iron oxides in Alfisols from a river terrace sequence of Mediterranean Spain, *Geoderma*, *33*, 283–296.

Reyes, I., and J. Torrent (1997), Citrate-ascorbate as a highly selective extractant for poorly crystalline iron oxides, *Soil Sci. Soc. Am. J.*, *61*, 1647–1654.

Scheinost, A. C., A. Chavernas, V. Barrón, and J. Torrent (1998), Use and limitations of second-derivative diffuse reflectance spectroscopy in the visible to near-infrared range to identify and quantify Fe oxides in soils, *Clays Clay Miner.*, *46*, 528–536.

Schwertmann, U. (1985), The effect of pedogenic environments on iron oxide minerals, *Adv. Soil Sci.*, *1*, 171–200.

Spassov, S., F. Heller, R. Kretzschmar, M. E. Evans, L. P. Yue, and D. K. Nourgaliev (2003), Detrital and pedogenic magnetic and mineral phases in the loess/palaeosol sequence at Lingtai (Central Chinese Loess Plateau), *Phys. Earth Planet. Inter.*, *140*, 255–275.

Tite, M. S., and R. E. Linington (1975), Effect of climate on the magnetic susceptibility of soils, *Nature*, *256*, 565–566.

Torrent, J. (1976), Soil development in a sequence of river terraces in northern Spain, *Catena*, *3*, 137–151.

Torrent, J., and A. Cabedo (1986), Sources of iron oxides in reddish brown soil profiles from calcarenites in southern Spain, *Geoderma*, *37*, 57–66.

van Oorschot, I. H. M., M. J. Dekkers, and P. Havlicek (2002), Selective dissolution of magnetic iron oxides with the acid-ammonium-oxalate/ferrous-iron extraction technique-II. Natural loess and paeosol samples, *Geophys. J. Int.*, *149*, 106–117.

Vidic, N., J. D. TenPas, K. L. Verosub, and M. J. Singer (2000), Separation of pedogenic and lithogenic components of magnetic susceptibility in the Chinese loess/palaeosol sequence as determined by the CBD procedure and a mixing analysis, *Geophys. J. Int.*, *142*, 551–562.

V. Barrón and J. Torrent, Departamento de Ciencias y Recursos Agrícolas y Forestales, Universidad de Córdoba, E-14071 Córdoba, Spain. (torrent@uco.es)

Q. Liu, School of Ocean and Earth Science, Southampton Oceanography Centre, Southampton S014 3ZH, UK.