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MÖSSBAUER STUDIES OF THE REDUCTION SPOTS IN WELSH PURPLE ROOFING SLATES

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ABSTRACT

A Mössbauer spectral study is reported of the chemistry of Fe in the bulk and in the pale green ellipsoids of purple slate from North Wales. Spectra of powered specimens were run in the transmission mode at room temperature. In the purple areas, ~80% of the iron is present as α-Fe_2O_3, the remainder occurring in the octahedral layers of chlorite with an Fe^{2+}:Fe^{3+} ratio of ~2.5:1. Spectra of several ellipsoids showed two doublets, a sharp one marking Fe^{2+} in chlorite and a broad one caused by Fe^{3+} ions on at least two different octahedral sites: the Fe^{2+}:Fe^{3+} ratio is ~2:1. The Mössbauer spectra offer no evidence in support of the accepted view that the ellipsoids were formed under reducing conditions, and it is possible that they were formed under non-reducing conditions.

RÉSUMÉ

Une étude spectrale de Mössbauer a été effectuée sur la chimie du Fe en vrac et du Fe dans les ellipsoïdes verts pâles des ardoises pourpres de North Wales. Des spectres de spécimens en poudre ont été soumis au mode de transmission, à la température de la pièce. Dans les régions pourpres, ~80% du fer se présente sous forme de α-Fe_2O_3 et le reste apparaît dans les couches octahédrales de chlorite avec un taux de Fe^{2+}:Fe^{3+} d'~2.5:1. Les spectres de plusieurs ellipsoïdes montraient deux doublets: un très aigu formant Fe^{2+} dans la chlorite et un large causé par les ions Fe^{3+} sur deux différents sites octahédrals: le taux de Fe^{2+}:Fe^{3+} est de ~2:1. Les spectres Mössbauer n'offrent aucune preuve confirmant le fait que les ellipsoïdes étaient formés sous des conditions réduites et qu'il est possible qu'ils aient été formés sous des conditions non-réduites.

(Traduit par le journal)

INTRODUCTION

The well-developed pale green ellipsoids in Welsh purple roofing slates have been referred to for more than a century as reduction spots (Maw 1868), presumably because the ellipsoids are devoid of the red hematite particles which contribute in a large measure to the purple colour of the bulk slate and, secondly, because ferrous-bearing silicates are often green. Typical ellipsoid dimensions are $x:y:z = 1.7:1:0.26$, where x is commonly one to three cm. They are useful indicators of the magnitudes of strains sustained by slates during deformation. Little is known of their chemistry or of the conditions under which they were formed. In this contribution, Mössbauer-derived ferrous: ferric concentration ratios for the chlorite component of slate are presented to show that the ellipsoids possibly were not formed under reducing conditions. The concentration of uranium in the reduced areas of sandstones (McKelvey *et al.* 1950) is an example of the economic potential of variegated strata.

RESULTS AND DISCUSSION

Figures 1 and 2 present, respectively, room-temperature Mössbauer spectra of powdered specimens of an ellipsoid and of a purple slate. Experimental details have been described previously (Manning & Tricker 1975). Spectra were fitted using Stone's programs (Stone 1967). The spectra are representative of several slates picked at random off beaches and roofs in the Aberystwyth area, except that in spectra of the deeper-purple slates the hematite peaks are more prominent. The main doublet in the ellipsoid spectra undoubtedly marks octahedral ferrous ions, probably in the chlorite component, with half-widths, isomer shifts (δ) and quadrupole splittings (Δ) of 0.35 $mm.s^{-1}$, 1.14 $mm.s^{-1}$ and 2.62 $mm.s^{-1}$ respectively, relative to Fe foil. The broad shoulder on the limb of the low-velocity ferrous peak (Fig. 1) is part of a doublet (peak half-width 0.65 $mm.s^{-1}$) marking ferric ions in at least two different octahedral positions. There are two octahedral layers in chlorite. Calculated values of δ and Δ are 0.43 $mm.s^{-1}$ and 0.73 $mm.s^{-1}$ respectively. Ferrous:ferric ratios for five spots in different slates are in the range 1.2:1 to 3:1, with an average value of 2:1.

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(Values of δ and Δ are in the range expected of the ions postulaed—Bancroft 1973). Broad absorptions of half-width 0.5 mm.s^{-1} in spectra of an oxyamphibole have been attributed to ferric ions in three different sites (Hawthorne & Grundy 1975).

Purple-slate spectra (Fig. 2) in the velocity range presented comprise three doublets, marking Fe^{3+} ions in hematite (the inner pair of a magnetic α-Fe_2O_3 six-line pattern), Fe^{2+} in chlorite and, although not obvious visually, Fe^{3+} in chlorite. The appearance of a Fe_2O_3 six-line pattern at 300°K indicates that nearly all hematite particles are >200Å in diameter (Ganges *et al.* 1973). Ferrous:ferric ratios of the purple areas are more difficult to measure accurately than in reduction spots because of the greater complexity of purple-slate spectra, but ratios of 2.5 (±1.5):1 were measured for four slates of different depths of colour. Values of δ and Δ are, within experimental error (±0.04 mm.s^{-1}), equal to those measured for ferrous and ferric ions in the ellipsoids. Clearly, Fe^{2+}:Fe^{3+} values are similar for the chlorite component of the purple areas and ellipsoids.

If ferric ions in chlorite are as easily reduced as those in hematite, these results would suggest that the ellipsoids were not formed under reducing conditions. Hence, organic matter and sulphides, materials that may comprise the dark nuclei of ellipsoids, are not involved as reducing agents. Carbonized matter was used extensively to reduce the iron (to ferrous) and so influence the colours of ancient ceramics (Hess & Perlman 1974).

Mössbauer spectra of grey and green slates measured in these laboratories are virtually identical, and Fe^{2+}:Fe^{3+} values are > 10:1. Chemical analyses (Deer *et al.* 1962) and optical absorption spectra (Faye 1968) of green unoxidized chlorites are consistent with high ratios. The low ratios for ellipsoids and for the purple slates and the presence of hematite in the purple areas seem to reflect oxidizing conditions at the time of deposition of the original mud and subsequent non-reducing conditions.

The ellipsoids and the purple areas are separated by a narrow dark-blue band of width ~0.1 mm. This band is probably low in the reddish form of hematite relative to the purple area. The deep-blue material contributes, with the hematite, to the purple colour. The blue colour is too intense to be attributed to crystal-field transitions within ferrous and ferric ions. Possible causes are $Fe^{2+} \rightarrow Fe^{3+}$ intervalence charge-transfer processes (Robbins & Strens 1972) in the red-end of the spectrum or the specularite form of hematite. Intervalence charge-transfer processes in the chlorite component can be eliminated because the forms of Fe are the same in the chlorite component of green and purple areas, whereas partly reduced iron oxides are likely to be black.

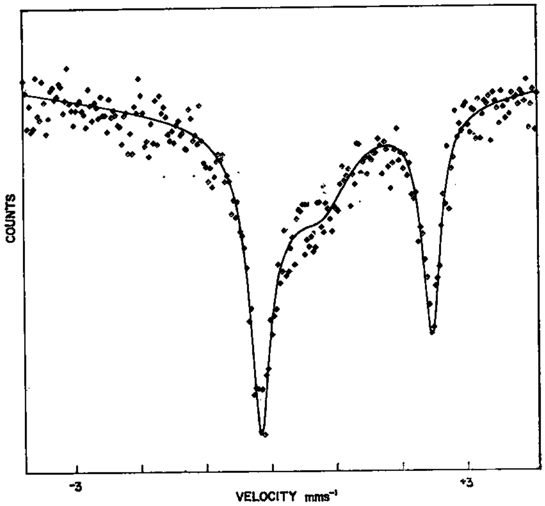

FIG. 1. Mössbauer spectrum of an ellipsoid containing 1% Fe. Continuous curve represents computer-generated best fit. χ^2 = 192 for 216 degrees of freedom. The Fe^{2+}:Fe^{3+} ratio for this specimen is 1.2:1. The noisy quality of this spectrum arises from a combination of low Fe values and the small amounts of material available.

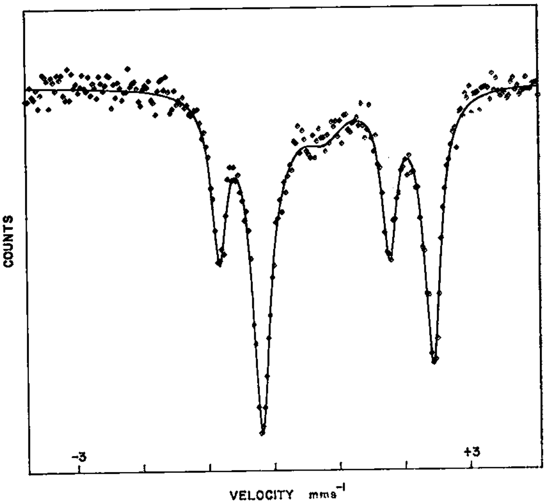

FIG. 2. Mössbauer spectrum of a purple slate containing 7% Fe. χ^2 = 234 for 230 degrees of freedom. The six-line pattern of Fe_2O_3 is not shown. Approximately 80% of the Fe is in Fe_2O_3.

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