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**Notes**

# Remagnetization and chemical alteration of sedimentary rocks

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**Abstract:** Chemical remagnetization is a very common phenomenon in sedimentary rocks and developing a greater understanding of the mechanisms has several benefits. Acquisition of a secondary magnetization is usually tangible evidence of a diagenetic event that can be dated by isolation of the chemical remanent magnetization and comparison of the pole position to the apparent polar wander path. This can be important because diagenetic investigations are frequently limited by the difficulty in constraining the time frames in which most past events have occurred. Remagnetization can commonly obscure a primary magnetization; developing a better understanding of remagnetization could improve our ability to uncover primary magnetizations. Many chemical remagnetization mechanisms have been proposed, including those associated with chemical alteration by a number of different fluids (orogenic, basinal and hydrocarbons), burial diagenetic processes (clay diagenesis and maturation of organic matter) or other processes. This paper summarizes our current knowledge of these chemical remagnetization mechanisms, with a focus on examples where there is a connection with chemical alteration.

Secondary magnetizations are common in sedimentary rocks and are widespread (e.g. McCabe & Elmore 1989). Since originally 'discovered' approximately 50 years ago, many palaeomagnetists have considered them a problem because they can obscure or remove primary magnetizations, which are commonly considered to be of greater interest. It is therefore important to better understand these secondary magnetizations in order to isolate primary magnetizations. Remagnetization or acquisition of a secondary magnetization can also be tangible evidence of a diagenetic event; remagnetizations can therefore be used to date diagenetic events. Diagenetic investigations can be limited by the difficulty in constraining the timeframes in which the events occurred. This dating approach is based on isolation of the chemical remanent magnetization (CRM) carried by diagenetic magnetic minerals and comparison of the pole position for the CRM to the appropriate apparent polar wander path (APWP). CRMs have also been used to constrain the timing of deformation (e.g. Stamatakos *et al.* 1996; Weil & Van der Voo 2002*a*). Magnetic susceptibility data and remagnetizations can also have applications in hydrocarbon exploration.

This Special Publication contains a selection of papers that focus on chemical remagnetization and magnetic changes associated with chemical alteration by hydrocarbons. In addition to several case studies, the book includes a paper on the history of remagnetization studies (Van der Voo & Torsvik 2012) as well as a number of review articles on various aspects of remagnetization. This introductory paper provides a general overview and reviews our current knowledge of chemical remagnetization mechanisms. We will not try to cover all papers on remagnetization, but will focus on examples where there is a connection with chemical alteration.

## Remagnetization mechanisms

Our understanding of remagnetization processes has improved significantly since the first hints of remagnetization in the 1950s and Creer's 'remagnetization hypothesis' (Creer 1968). Dating of diagenetic events using palaeomagnetism has also met with varying degrees of success (see below). Although we have significantly improved our understanding of chemical and other remagnetization mechanisms, the origins of some remagnetizations remain enigmatic.

Many secondary magnetizations are interpreted to be chemical or diagenetic in origin, although other remagnetization mechanisms (e.g. thermoviscous) are also important (e.g. Kent 1985; Hudson *et al.* 1989). Evidence cited in support of the chemical origin includes authigenic magnetic phases in the rocks (e.g. Elmore *et al.* 1985; Suk *et al.* 1990) and thermal maturities which are too low for a thermoviscous remagnetization based on blocking-temperature–relaxation-time relationships (e.g. Pullaiah *et al.* 1975; Jackson 1990; Dunlop *et al.*

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2000). Rock magnetic data has also been cited as supporting a diagenetic origin for some magnetite (e.g. Jackson 1990; Jackson & Sun 1992). See Jackson & Swanson-Hysell (2012) for an update on this issue.

As described in the following sections, many chemical remagnetization mechanisms have been proposed. All involve alteration by fluids with a number of different driving mechanisms or sources for the fluids suggested, including tectonic processes, diagenetic reactions, and heat from igneous bodies. In this paper the chemical remagnetization mechanisms are divided into two general groups: alteration triggered by externally derived fluids and alteration associated with burial diagenetic processes. Tests of these remagnetization mechanisms are important in order to demonstrate a connection between a diagenetic event and a specific remagnetization, and thereby date a diagenetic event. For example, determining that a remagnetization is caused by fluids requires testing for a connection between the alteration caused by a particular fluid and a CRM. A basic approach is to conduct a presence/absence test where geochemical and petrographic data are compared with the distribution of a CRM (e.g. Elmore *et al.* 1985, 1994; Symons *et al.* 2005). A more powerful approach is to conduct a contact test around veins (Figs 1 & 2; Cochran & Elmore 1987; Elmore *et al.* 1993*a*) or conduits for fluid flow (Fig. 3; Elmore *et al.* 1998, 2010; Costanzo-Álvarez *et al.* 2000*a*; Evans *et al.* 2012). In this test, petrographic, geochemical, and palaeomagnetic data are collected and compared from in and around the fluid conduit (Fig. 2). If the geochemical evidence for alteration coincides with the distribution of a CRM, a strong case for a connection between the fluid which caused the alteration and the CRM is possible.

## Externally derived fluids

### *Orogenic fluids*

The action of orogenic fluids is a popular mechanism invoked for many CRMs (McCabe & Elmore 1989). For example, many Late Palaeozoic CRMs in North America are inferred to be related to alteration caused by fluids which migrated from the Appalachian and Ouachita fold-thrust belts (e.g. Oliver 1986, 1992). These fluids probably migrated along aquifers (e.g. Bethke & Marshak 1990) as a result of compression (e.g. squeegee model of Oliver 1992) or by gravitational flow of meteoric fluids from mountains (e.g. Bethke & Marshak 1990; Garven 1995).

Evidence supporting the hypothesized connection between orogenic fluids and remagnetization is a temporal association between the timing of many CRMs and orogenies as well as a spatial association between the CRMs and mountain belts

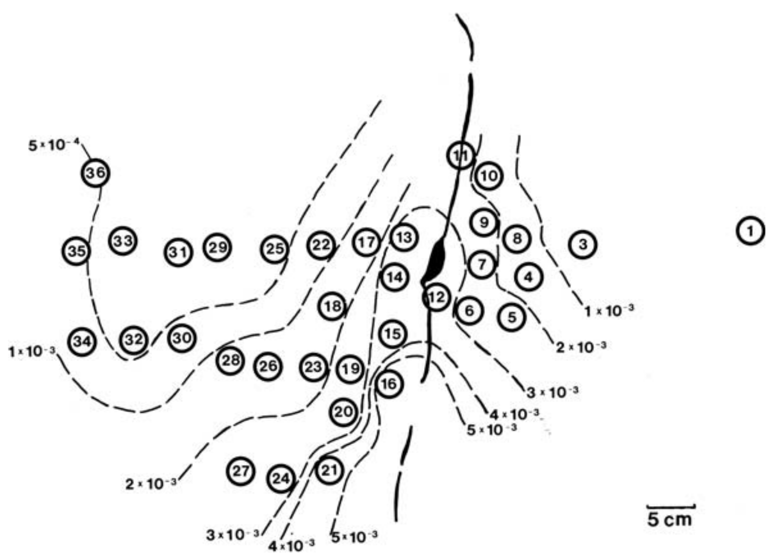


**Fig. 1.** Natural remanent magnetization ($Am^{-1}$) intensities decrease away from calcite-filled fractures in the Ordovician Kindblade Formation in southern Oklahoma. The highest intensities correspond to maximum amount of liesegang banding which is caused by haematite. Reddish specimens near the veins contain a post-tilting Permian CRM in haematite, whereas specimens away from veins contain an unstable and weak magnetization. These results suggest that the CRM was caused by the fluids which migrated away from the veins (after Cochran & Elmore 1987).

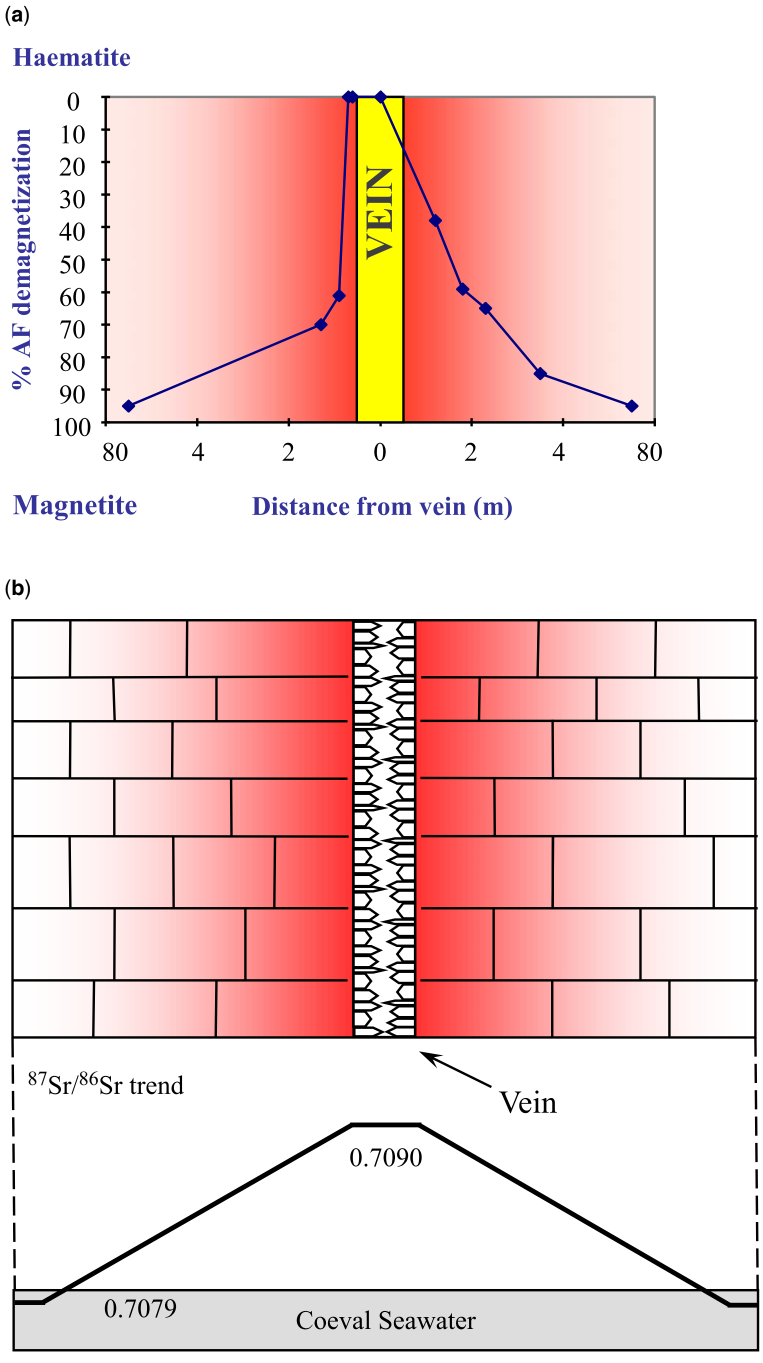


**Fig. 2.** (**a**) Vein in the Ordovician Viola Limestone (southern Oklahoma) showing distance from the vein v. percent alternating field (AF) decay. The rock near the vein contains a Permian CRM in haematite whereas the rock away from the vein contains a Pennsylvanian CRM in magnetite (Elmore *et al.* 1993*a*). The increase in AF decay away from the vein shows that the haematite CRM decreases with distance from the vein, whereas the magnetite CRM increases with distance from the vein. (**b**) Schematic diagram illustrating remagnetization and geochemical halos around a vein. The coincidence of the two halos suggests that they are related and that the CRM in haematite dates the migraton of fluid through the veins and the associated geochemical alteration.

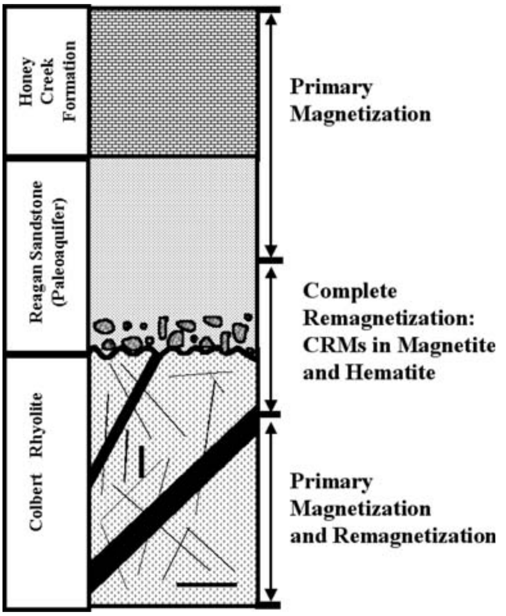


**Fig. 3.** Stratigraphic section showing the Colbert Rhyolite (with intruded dykes), Reagan Sandstone, and Honey Creek Limestone in the Arbuckle Mountains (southern Oklahoma), which illustrates the distribution of the primary and secondary components found in the units. The occurrence of the secondary magnetizations within and below the palaeoaquifer suggests that fluids that moved through the Reagan Sandstone caused the remagnetization events. Modified after Elmore *et al.* (1998).

(e.g. McCabe & Elmore 1989). Older CRMs in the southern Appalachians and younger CRMs in the north is consistent with the south to north progression of Alleghanian deformation and with the hypothesis that orogenic fluids caused remagnetization (e.g. Miller & Kent 1988). In the central Appalachians, post-folding remagnetizations near the hinterland, syntilting remagnetizations in the central part of the belt and pre-folding remagnetizations near the foreland were interpreted to be consistent with brine migration (Stamatakos *et al.* 1996). Migration of orogenic fluids has also been proposed as an explanation for some regional trends in magnetite authigenesis (e.g. Jackson *et al.* 1988; McCabe *et al.* 1989; Lu *et al.* 1991; Saffer & McCabe 1992).

Syntilting CRMs have been related to alteration caused by fluids activated during deformation (e.g. McCabe *et al.* 1983). In the Valley and Ridge province in West Virginia, the Devonian Helderberg Group (an aquitard) and the overlying Oriskany Formation (a palaeoaquifer) both contain similar syntilting Late Palaeozoic CRMs residing in magnetite (Elmore *et al.* 2001). The Oriskany contains geochemical and fluid inclusion evidence consistent with alteration by orogenic fluids. In contrast, the fluid inclusion and geochemical data (e.g. coeval $^{87}Sr/^{86}Sr$ values) from the Helderberg indicate only *in situ* fluids and the CRM is interpreted to have been acquired by another remagnetization mechanism such as a burial diagenetic process.

Dennie *et al.* (2012) report results from oriented drill core from the Mississippian Barnett Shale, a primary source rock and the major unconventional gas reservoir in the Fort Worth Basin, Texas. The shale contains a magnetization with shallow inclinations and streaked SE–S-directed declinations which are attributed to several CRMs. Specimens from around some veins contain Permian–Triassic CRMs, and elevated $^{87}Sr/^{86}Sr$ ratios and S isotope results from vein minerals suggest the CRMs could be related to fluids sourced from the Ouachita thrust front that forms the eastern margin of the basin.

In a regional study of Palaeozoic rocks in the southern Canadian Cordillera, Enkin *et al.* (2000) report the presence of a pervasive pre-folding Cretaceous CRM in magnetite which was older in the western part of the thrust belt than in the eastern part, as well as a syntilting to post-tilting thermoviscous remagnetization in magnetite. They suggested that the magnetite CRM was acquired prior to deformation in response to an eastward-migrating diagenetic front (Fig. 4). Zechmeister *et al.* (2012) report that folds within Mississippian carbonates in the southern Canadian Cordillera contain a similar pre-tilting Cretaceous CRM residing in magnetite. Fluid contact tests and geochemical data from around pre-deformational bedding-parallel veins show a direct correlation to the magnetite CRM. An intermediate-temperature late syntilting to post-tilting Tertiary CRM residing in pyrrhotite is also present. Based on the presence of thermal sulphate reduction (TSR) byproducts, the pyrrhotite CRM is interpreted to be the result of late-stage TSR of hydrocarbons that were exposed to warm fluids which migrated along faults and fractures. In contrast to examples where CRMs occur around fluid conduits, Evans *et al.* (2012) report that the Devonian Alamo Breccia (Nevada), a likely palaeoaquifer, was not a conduit for focused flow of remagnetizing fluids. Evans *et al.* (2012) suggest that externally derived fluids moved pervasively through the rocks, causing acquisition of a CRM in the Late Palaeozoic Era (Sonoma Orogeny?).

Many studies have also interpreted that CRMs were caused by orogenic fluids in areas other than North America. The role of orogenic fluids was evaluated for Late Palaeozoic CRMs in Europe (e.g. Weil & Van der Voo 2002*b*; Zegers *et al.* 2003). Font *et al.* (2012) summarize remagnetization in

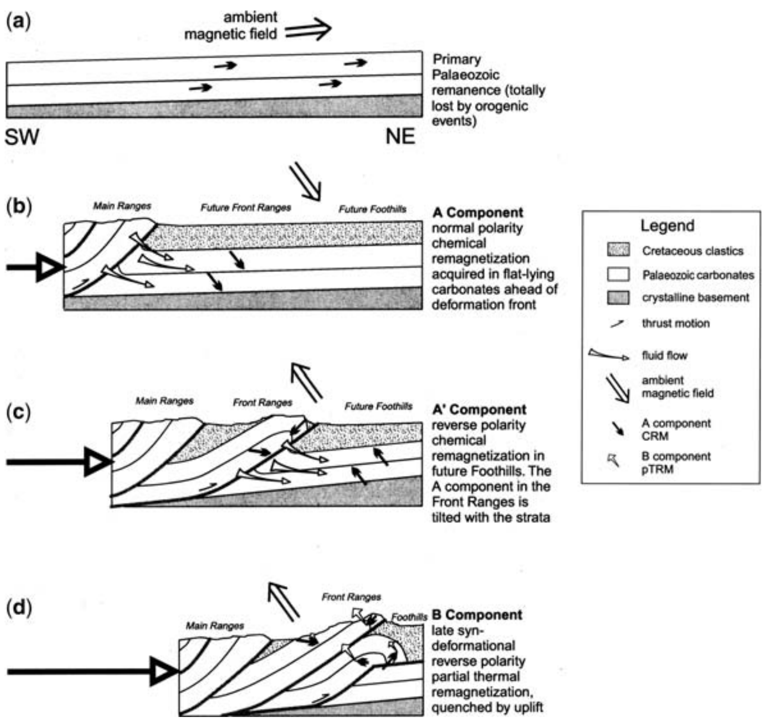


**Fig. 4.** Simplified diagram modelling magnetization acquisition in the southern Canadian Cordillera (after Enkin *et al.* 2000). (**a**) Shallow-inclination Palaeozoic remanence acquired in carbonates. (**b**) A component: Ahead of the eastward migrating deformation front, carbonates in the future Front Ranges acquire total chemical remagnetization with steep downwards direction. (**c**) Before the Front Ranges become entrained into the deformation front, the A component becomes fixed and rotates with the beds. A′ component: After a polarity reversal, a similar event remagnetizes the carbonates which form the Foothills. (**d**) Structures underneath the frontal thrusts of the Front Ranges uplift the Front Ranges and Foothills and, during one reverse-polarity chron, quench a partial thermal remanence acquired during burial. CRM: chemical remanent magnetization; pTRM: partial thermo-remanent magnetization.

South America, and report several remagnetization events related to major tectonic episodes.

Several palaeomagnetic-geochemical studies provide evidence that warm, saline fluids caused remagnetization in and around conduits for flow (Elmore *et al.* 1993*a*, 1998). The timing of these CRMs does not necessarily indicate that they are orogenic fluids. For example, the results of a study of the Viola Limestone in southern Oklahoma suggest that basinal fluids locally caused a Permian CRM in haematite within altered rock around veins which were the conduits for externally derived fluids (Fig. 2; Elmore *et al.* 1993*a*). The rock away from the veins was not altered by such fluids and contains a Pennsylvanian CRM in magnetite that was interpreted to be caused by a burial diagenetic mechanism. In another study in southern Oklahoma, the Upper Cambrian Reagan Sandstone (the basal palaeoaquifer in the Palaeozoic section) contains two Late Palaeozoic CRMs that can be related to fluid migration (Fig. 3; Elmore *et al.* 1998); rocks above and below contain primary or early magnetizations, however. Other studies in the Arbuckle Mountains in Oklahoma document that basinal fluids migrated laterally through palaeoaquifers and vertically through faults/fractures causing localized remagnetization and alteration in and around the fluid conduits during a time interval of *c.* 60 Ma in the Late Palaeozoic (Elmore 2001). The fact that some CRMs reside in haematite whereas others reside in magnetite indicates that remagnetization was caused by fluids with different chemistries.

Numerous studies have investigated CRMs in fault zones, relating them to igneous activity or to extensional tectonics (e.g. Torsvik *et al.* 1992; Preeden *et al.* 2009). A study of the Moine Thrust Zone (MTZ) in the Caledonides of Scotland suggests that four focused fluid-flow events occurred along the MTZ between the Devonian and Early Cenozoic (Blumstein *et al.* 2005). The localized CRMs coincide with post-Caledonian events such as the migration of hydrothermal fluids related to Devonian igneous activity; regional crustal extension of Scotland and NW Europe in the Permian; Proto-Atlantic rifting in the Triassic; and Tertiary intrusive activity. Red fault-related breccias with abundant authigenic haematite in the Cambro-Ordovician Durness Group in NW Scotland that are found in close proximity to the MTZ contain two CRMs (Elmore *et al.* 2010). The host Durness (grey dolomite) contains a Devonian CRM (Fig. 5) in magnetite. North–south veins contain a Triassic CRM whereas east–west veins contain a Jurassic CRM (Fig. 5), both of which reside in haematite. The two CRMs are interpreted as reflecting two separate fluid-flow events that precipitated authigenic haematite and caused brecciation during extension of the NE Atlantic margin. A study of the Highland Boundary Fault (HBF) in Scotland suggests there were multiple flow events along the fault in the Late Palaeozoic (Elmore *et al.* 2002). The Devonian Old Red Sandstone in the vicinity of the Great Glen Fault in Scotland contains two different components residing in haematite: a post-tilting Carboniferous CRM in the Loch Ness area and a Cretaceous or Triassic CRM to the NE (Elmore *et al.* 2006*a*). The presence of different CRMs residing in haematite along different segments of the faults is similar to that reported from other studies of faults in Scotland (e.g. Van der Voo & Scotese 1981; Torsvik *et al.* 1983; Tarling 1985). These and other studies provide evidence that fault zones can be conduits for localized fluid-flow events at different times and thereby control the distribution of diagenetic alteration, mineralization and remagnetization.

A number of studies present evidence for connections between CRMs and basinal-type or hydrothermal fluids. For example, in the Western Canada Basin several studies have suggested that CRMs are related to dolomitization (Symons *et al.* 1999) and recrystallization in dolomites (Cioppa *et al.* 2000). Results from the NE Williston Basin (Szabo & Cioppa 2012) indicate the presence of a Jurassic remagnetization in magnetite that is interpreted to have been caused by basement fluids. These fluids

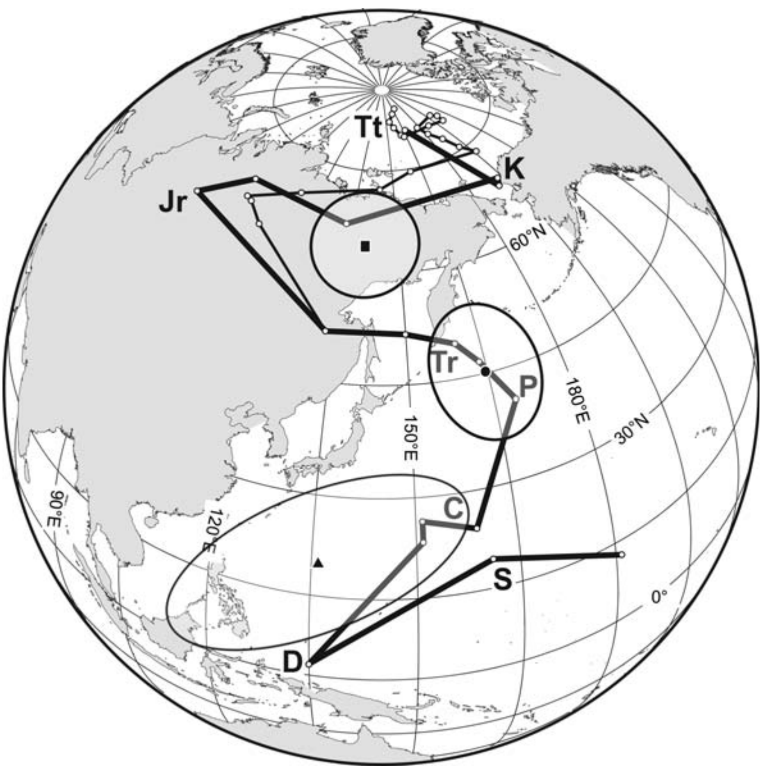


**Fig. 5.** Poles (with 95% error ellipses, dp and dm) from the red breccias and host dolomite in Scotland on the apparent polar wander paths from Van der Voo (1993) for the Phanerozoic (heavy line with circles representing the median age poles) and Besse & Courtillot (2002) for the last 200 Ma (thinner line with circles representing the 10 Ma mean poles). CRM1: triangle, Durness Group Dolomite; CRM2: circle, north–south veins; and CRM3: square, east–west veins (after Elmore *et al.* 2010).

moved along faults and fractures that formed as a result of the Hartney impact/volcanic structure and/or tectonic activity in the Superior Boundary Zone. Harlan *et al.* (1996) report a Late Cretaceous CRM in mafic dykes in Montana that is attributed to alteration by hydrothermal fluids.

### *Mineralizing fluids*

Many studies have used palaeomagnetism to date or constrain the timing of Mississippi Valley Type (MVT) deposits (e.g. Symons *et al.* 1996; Leach *et al.* 2001; Zegers *et al.* 2003). This approach is based on the hypothesis that the mineralizing fluids cause precipitation of magnetic phases (magnetite and pyrrhotite); see Symons *et al.* (1996) for a summary of the palaeomagnetic dating approach and for the results from a number of MVT deposits. Several studies have shown that the host rocks have distinct and older magnetizations than the mineralized rocks, which suggest that the ore magnetization is related to the mineralizing fluids (e.g. Lewchuk & Symons 1995; Symons *et al.* 2005). Many of the MVT deposits are interpreted to have formed from orogenic fluids that were triggered as a result of tectonic activity (Leach *et al.* 2001). The palaeomagnetic data from some MVT deposits have a streaked or oval distribution rather than a circular distribution (Lewchuk & Symons 1995). Although there are several possible explanations (e.g. overlapping components), one hypothesis is that the streaked pattern reflects apparent pole wander during the acquisition of the CRM (Lewchuk & Symons 1995).

### *Weathering fluids*

A number of studies present evidence that weathering fluids can cause remagnetization. Examples include Mesozoic limestones in Germany where goethite has been shown to carry a secondary remanence (Heller 1979; Johnson *et al.* 1984). Loucks & Elmore (1986) present evidence that surficial dedolomitization can cause a remagnetization in goethite. Meteoric/weathering fluids can cause a localized remagnetization in haematite around karst features (Nick & Elmore 1990).

Remagnetization by weathering is currently experiencing a surge in interest related to Late Carboniferous–Triassic remagnetizations, common in alteration zones below palaeoweathering surfaces in crystalline basement rocks in Europe (e.g. Edel & Schneider 1995). Many of these remagnetizations reside in authigenic haematite and are interpreted to be caused by weathering fluids (e.g. Ricordel *et al.* 2007; Franke *et al.* 2010; Fàbrega *et al.* 2012). A study of dolomite veins in the Precambrian–Early Palaeozoic Dalradian schist in Scotland reported a Carboniferous–Triassic CRM which was interpreted as being related to deep oxidizing weathering (Parnell *et al.* 2000). Late Palaeozoic remagnetizations residing in haematite are also reported from crystalline rocks in North America and have been related to weathering fluids (Hamilton *et al.* 2012) or to migration of brines along porous zones at the Precambrian–Carboniferous nonconformity (Geissman & Harlan 2002).

### *Hydrocarbons*

Numerous studies provide evidence for, or propose a relationship between, hydrocarbons and authigenic magnetite and/or pyrrhotite (e.g. Elmore *et al.* 1987, 1993*b*; McCabe *et al.* 1987; Reynolds *et al.* 1993; Cioppa & Symons 2000; Aldana *et al.* 2003; Costanzo-Álvarez *et al.* 2006). In some cases the magnetite or pyrrhotite carries a CRM (e.g. Benthien & Elmore 1987; Elmore & Crawford 1990; Elmore & Leach 1990; Gose & Kyle 1993; Katz *et al.* 1996; Lewchuk *et al.* 1998). Some studies have presented evidence that secondary magnetite could be responsible for magnetic enhancement in soil polluted by hydrocarbons (Rijal *et al.* 2010). Pyrrhotite can also form during thermochemical sulphate reduction of hydrocarbons (Pierce *et al.* 1998); this has been proposed as a mechanism for acquisition for a CRM in pyrrhotite (Manning & Elmore 2012; Zechmeister *et al.* 2012). In some hydrocarbon-impregnated units, magnetite is present but it does not carry a stable remanence; in some red beds, hydrocarbons can cause a net decrease in magnetization by dissolving haematite (e.g. Kilgore & Elmore 1989; Elmore & Leach 1990). Several studies also describe the chemical conditions in which magnetite can form in association with hydrocarbons (e.g. Machel 1995).

Based on this connection between magnetic anomalies and hydrocarbon micro-seepage, it has been proposed that petroleum reservoirs can be characterized based on the analysis of near-surface and secondary magnetic contrasts in high-resolution aeromagnetic surveys over oil fields. Donovan *et al.* (1979) identified pronounced noticeable aeromagnetic anomalies in the Cement oil field (Oklahoma). They associated these anomalies with the presence of authigenic magnetite produced by the chemical alteration of original Fe-oxides in a reducing environment produced by the underlying oil reservoir. Although aeromagnetic anomalies could also be due to other factors related to natural or anthropogenic processes (Gay 1992), a hydrocarbon-related origin is possible in geological settings dominated by underlying oil reservoirs. Donovan *et al.* (1984), Foote (1996) and Saunders *et al.* (1991) have argued that it is possible to use aeromagnetic studies to determine the presence of hydrocarbon reservoirs.

Studies utilizing bulk magnetic properties (e.g. magnetic susceptibility) measured in soils, sediments and drill cuttings can provide a better understanding and assessment of the origin of the magnetic anomalies (Aldana *et al.* 1999, 2003; Costanzo-Álvarez *et al.* 2000*b*, 2006; Díaz *et al.* 2000; González *et al.* 2002). It is crucial in these types of studies to analyse for and rule out contamination via anthropogenic factors. Some studies, based on the presence of spherical aggregates of magnetic minerals which points to an *in situ* formation, show that it is possible to discriminate between magnetic susceptibility anomalies related to hydrocarbon micro-seepage and those caused by lithological contrasts, that is sedimentation processes (Costanzo-Álvarez *et al.* 2000*b*).

Using magnetic properties of drill cuttings taken at shallow depth levels, Guzmán *et al.* (2011) gave a preliminary characterization of an exploratory area in the Maturin Sub-Basin, Venezuela. They mapped magnetic susceptibility and the S-ratio, as well as the concentration of free radicals in the extracted organic matter measured using Electron Paramagnetic Resonance (EPR) experiments (see Díaz *et al.* 2000), from drill cuttings. These maps show a region of anomalous values, probably associated either with the maximum accumulations of an unexplored deep reservoir and/or with the path of migrated hydrocarbons. They argue that this result could be employed for future exploration and production ventures in the region, in a similar way as seismic attributes are used in the oil industry to monitor the continuity of a particular sedimentary layer and/or features associated with hydrocarbon accumulations. Due to their low cost and non-invasive nature, magnetic methods can be used as an alternative tool to study the near-surface expression of hydrocarbon micro-seepage not only in oil fields but also in prospective areas (González *et al.* 2002).

The rock magnetic characterization of the stratigraphic well (Saltarín 1A) reports early and late diagenetic events that affected the Upper Cretaceous–Pliocene sequence of the distal Llanos foreland basin in Colombia (Costanzo-Álvarez *et al.* 2012). At shallow depths, anomalously high susceptibility values appear to be the result of partial replacement of pyrite framboids by magnetite. At deeper levels the magnetic anomaly observed is related to variation from oxidized palaeosols to alluvial plain sediment which accumulated in reducing conditions. This suggests a pedoclimatic control.

Emmerton *et al.* (2012) found an inverse correlation between the magnetic susceptibility and the extracted organic matter content for samples from the Wessex Basin in SW England. These results indicate a complex relationship between existing magnetic minerals within the sandstones and the alteration of these magnetic minerals due to the multiplex biological activity and biodegradation of the oil.

Magnetic properties from drill cuttings were compared with petrophysical properties from an oil well in the Golfo San Jorge Basin, Argentina (Mena & Walther 2012). Positive correlations were found between bulk magnetic susceptibility and relative hydrocarbon content, and between magnetic properties and neutron log porosity. A negative correlation exists between concentration indices for some magnetic species (magnetite and pyrrhotite) and resistivity. Pyrrhotite could be directly related to the presence or migration of hydrocarbons in porous units. The qualitative correlations between magnetic data and key petrophysical parameters suggest the potential utility of these techniques for subsurface exploration.

## Burial remagnetization mechanisms

Although the migration of externally derived fluids is a likely agent for many remagnetizations, widespread CRMs that occur in rocks that have not been altered by such fluids must be explained by other remagnetization mechanisms. Several burial diagenetic processes, such as clay diagenesis and maturation of organic matter, have received considerable attention as agents of remagnetization. These mechanisms can be thought of as ‘cooking in their own juices’.

### *Smectite to illite*

A number of studies have proposed that the transformation from Fe-rich smectite to illite can release iron that can result in magnetite authigenesis (e.g. Lu *et al.* 1991; Hirt *et al.* 1993; Katz *et al.* 1998, 2000; Gill *et al.* 2002; Woods *et al.* 2002; Zegers *et al.* 2003; Blumstein *et al.* 2004; Moreau *et al.* 2005; Tohver *et al.* 2008). Many of these studies incorporated presence/absence tests (e.g. Katz *et al.* 2000; Gill *et al.* 2002; Woods *et al.* 2002). Weil & Van der Voo (2002*b*) noted the presence of microscale Fe oxides in a matrix of Fe-rich smectite and aluminous illite.

In a study of Mesozoic carbonates in the Vocontian Trough in SE France, the results support a hypothesized acquisition of a CRM residing in magnetite during burial diagenesis of smectite (Katz *et al.* 1998, 2000). Where smectite has altered to other clay minerals, conglomerate tests indicate that the magnetization is secondary and tilt tests indicate that the limestones contain a pre-tilting magnetization, interpreted as a CRM. Where significant smectite is still present, the CRM is absent/weakly developed (Fig. 6) and where the clays show no evidence for burial alteration, the units are

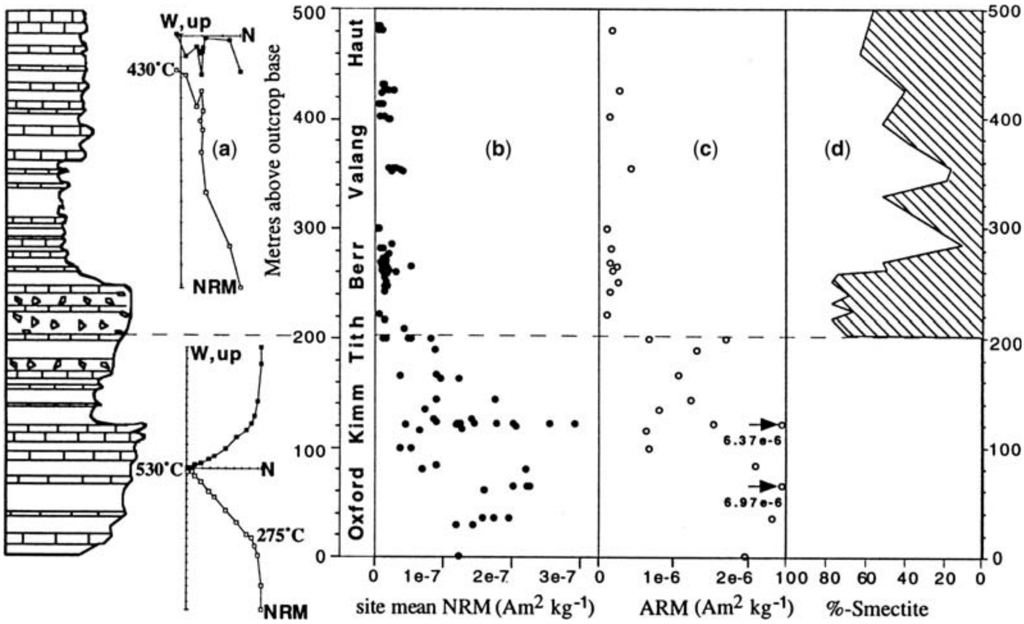


**Fig. 6.** Results from central part of Vocontian trough near Montclus as a function of stratigraphic position (left column; limestone, hachured; marl, blank; breccia, spotted). (**a**) Orthogonal projection diagrams for representative specimens (tilt-corrected) from younger units (top) and from older units (bottom). Most specimens from the older units contain a well-developed CRM. Closed symbols: horizontal projection; open symbols: vertical projection. (**b**) The natural remanent magentization (NRM) as a function of stratigraphic position. Intensities are higher in older units where the CRM is well developed. (**c**) Anhysteretic remanent magnetization (ARM) as a function of stratigraphic position is shown, indicating that older units contain more remanence-carrying magnetite. (**d**) The column on the right shows percent smectite of total clay fraction (after Katz *et al.* 1998).

characterized by a primary magnetization. The rocks with this CRM have $^{87}Sr/^{86}Sr$ values that are similar to coeval seawater; externally derived fluids are therefore not a likely agent of remagnetization.

While geochemical and petrographic studies provide important clues for establishing this relationship, the ultimate test of this hypothesis requires the application of independent dating methods to verify the palaeomagnetic ages. K–Ar dating of illite is one such approach that has worked in some cases (e.g. Elliot *et al.* 2006*a*; Tohver *et al.* 2008; Zwing *et al.* 2009), but in other cases it was not successful because of the presence of detrital illite (Elliot *et al.* 2006*b*).

Results of laboratory experiments provide evidence for a connection between authigenic magnetite and transformation of Fe-rich smectite to illite (Hirt *et al.* 1993). Other experimental studies (Cairanne *et al.* 2004; Moreau *et al.* 2005; Aubourg *et al.* 2008; Aubourg & Pozzi 2010) have presented evidence that low-temperature (95–250 °C) burial heating can cause acquisition of a CRM in magnetite. Aubourg *et al.* (2012) propose that burial remagnetization is continuous with greigite forming at or soon after deposition, magnetite at depths greater than 2 km and pyrrhotite at depths greater than 6 km.

## *Maturation of organic matter*

A number of studies provide evidence for a relationship between remagnetization and maturation of organic matter. For example, in a regional study of the Belden Formation, Colorado, Banerjee *et al.* (1997) reported that the timing of CRM acquisition is different across the basin and it agrees with the modelled time of maturation of organic matter for different localities. In addition, the oxygen isotopic data indicate that the diagenetic magnetite in the Belden formed from water having $\delta^{18}O$ near $0^{o}/_{oo}$ or less, implying a meteoric or connate source rather than a highly evolved orogenic or basinal fluid (Ripperdan *et al.* 1998). The results of these studies are consistent with a study of a single fold in the Belden which indicates that a syntilting CRM which resides in authigenic magnetite that rims pyrite grains (Fig. 7) is not related to syndeformational orogenic fluids (Fruit *et al.* 1995). A study of the Mississippian Desert Limestone and Chainman Shale (Blumstein *et al.* 2004), source rocks in

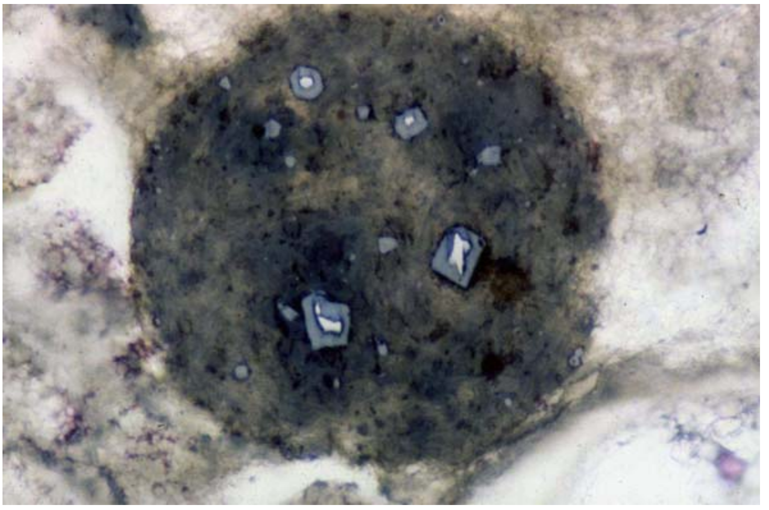

**Fig. 7.** Photomicrograph of a fecal pellet from the Belden Formation in reflected light. The pellets contain pyrite rimmed by magnetite. Pellet is 250 µm in diameter (after Fruit *et al.* 1995).

western Utah, found a Jurassic CRM that was interpreted to have formed as a result of the maturation of organic matter based on the overlap between the timing of CRM acquisition and the timing of oil generation from modelling studies (Fig. 8). The study also found that the timing of CRM acquisition did not overlap the timing of illitization based on kinetic modelling. In another study, the timing of a CRM in organic-rich beds in the Old Red Sandstone in Scotland agrees with independent estimates for the timing of thermal maturation (Plaster-Kirk *et al.* 1995). Other studies have also proposed a relationship between thermal maturity and remagnetization (e.g. Cioppa *et al.* 2002; Font *et al.* 2006).

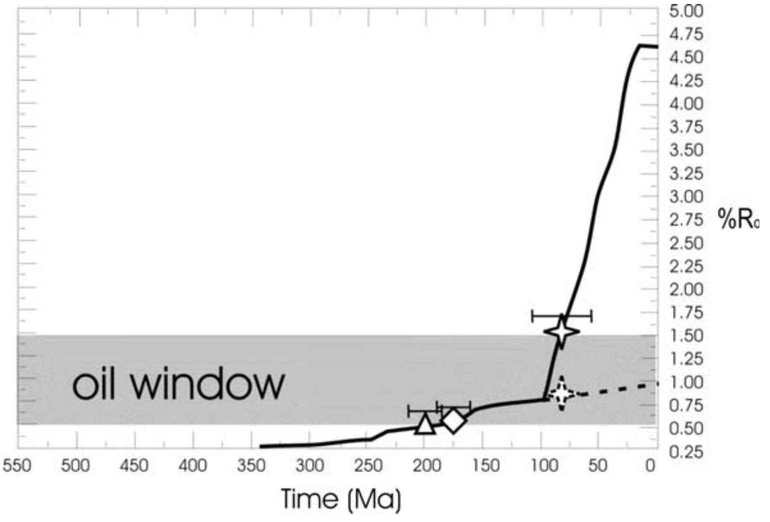


**Fig. 8.** Time versus vitrinite reflectance curve for the Mississippian Desert Limestone (with the oil window) and poles from the Desert Limestone/Chainman shale. The triangle (CR) and diamond (MHR) represent the Late Triassic–Early Jurassic component 1, and the star represents the Cretaceous–Early Tertiary component 2. Error bars for the poles were estimated from the APWP. The dashed line represents the estimated burial curve for the Chainman Shale in western Utah and the dashed star represents component 2 on the estimated curve, suggesting that component 2 could have been acquired within the centre of the oil window (modified after Blumstein *et al.* 2004).

Laboratory simulation experiments have also successfully produced magnetite by dissolution–reprecipitation of pyrite (Brothers *et al.* 1996). These experiments may simulate diagenesis at temperatures below 100 °C, one possible pathway for magnetite authigenesis. A study of organic-rich Jurassic sedimentary rocks adjacent to a Tertiary dyke in Scotland, considered as an analogue for burial heating, suggests that moderate burial depth might be sufficient to cause magneto-chemical changes (Katz *et al.* 1998).

It is important to note that the smectite to illite transformation and maturation of organic matter mechanisms for CRM acquisition are not necessarily mutually exclusive. Organic matter is intimately associated with clay minerals in black shales (Kennedy *et al.* 2002) and it is conceivable that the authigenesis of magnetic phases is facilitated by this interplay.

## Origin of magnetization in red beds

The reader is referred to Van der Voo & Torsvik (2012) for a summary of the history of the red bed debate. Some Mesozoic red beds contain a detrital remanent magnetization (DRM; e.g. Herrero-Bervera & Helsley 1983; Shive *et al.* 1984) and detrital specularite has been demonstrated as carrying a DRM in some Appalachian red beds (e.g. Kent & Opdyke 1985). Other red beds contain an early CRM that probably formed as a result of the breakdown of unstable Fe-bearing detrital grains such as hornblende and biotite (e.g. Butler 1992). Many other studies report Permian CRMs in Early and Middle Palaeozoic red bed units from the Appalachians that were deformed during the Alleghenian Orogeny (e.g. Kent & Opdyke 1985; Miller & Kent 1986; Miller & Kent 1988). It has been popular to relate the CRMs in some red beds to the actions of migrating orogenic fluids (e.g. McCabe & Elmore 1989). Many of these CRMs are found in rocks that do not contain evidence for such fluids (e.g. Cox *et al.* 2005) however, and their origins remain elusive.

## Origin of syntilting CRMs

Syntilting magnetizations are statistical observations that suggest that magnetizations were acquired during folding. Several possibilities exist for the origin of these magnetizations including: growth of new magnetic minerals during folding, physical rotation of magnetic minerals during folding (e.g. Kligfield *et al.* 1983; Hirt *et al.* 1986; van der Pluijm 1987; Kodama 1988), acquisition of a peizoremanent magnetization (PRM) (Xu & Merrill 1992; Borradaile & Jackson 1993; Borradaile 1997), and contamination by overlapping components (e.g. Hudson *et al.* 1989). In terms of the growth of new magnetic grains during folding, a true syntilting CRM could be produced. Determining the time of growth during folding is difficult because syntilting results observed in incremental tilt tests do not give a unique result. Growth of new minerals is commonly invoked for many syntilting CRMs, although specific chemical mechanisms are rarely demonstrated. In terms of the other three mechanisms, they will produce a false syntilting result or will completely reset the magnetization.

Remanence-carrying Fe oxide grains may rotate during folding, which would alter the original magnetic direction. The rotated direction would not be related to the ambient field during folding. Based on modelling, Kodama (1988) proposed that shear strain during flexural flow folding could cause a prefolding magnetization to be rotated into a syntilting configuration. Other studies also indicate that strain could account for the syntilting characteristics in some clastic units (e.g. Stamatakos & Kodama 1991). On the other hand, Kodama (1988) determined that volume-loss strain (solution) could not account for the observed syntilting character in one carbonate unit.

Several studies have tested for alteration of a CRM by comparing the magnetic properties between limestones with strain indicators. For example, Lewchuk *et al.* (2003) and Elmore *et al.* (2006*b*) tested for a connection between strain and remagnetization by comparing the types and levels of strain with the magnetic properties between the generally coarse-grained thickly bedded Helderberg and the thinly bedded and finer-grained Tonoloway in West Virginia. Standard tilt tests, as well as optimal differential untilting, from two anticlines indicate that the Helderberg contains a pervasive late syntilting CRM. The Tonoloway however contains a well-defined early syntilting CRM1 as well as a CRM2 which is similar to the CRM in the Helderberg. The CRMs reside in magnetite and rock magnetic results from the two units are similar, although the Helderberg samples have a finer apparent grain size (perhaps as a result of magnetic hardening). Pressure solution strain is higher in the Helderberg and lower in the Tonoloway. Strain may have caused rotation of magnetic minerals but it is not clear that the differences in strain between the units were high enough to cause the rotations that are needed to explain the tilt test results. Another viable hypothesis is a strain-enhanced chemical process caused dissolution and precipitation of new magnetite in solution structures during folding (e.g. Evans & Elmore 2006).

Folds with different geometries and tilted thrust sheets in the Mississippian rocks in Montana (O'Brien *et al.* 2007) all have the same magnetic characteristics and are probably caused by the same

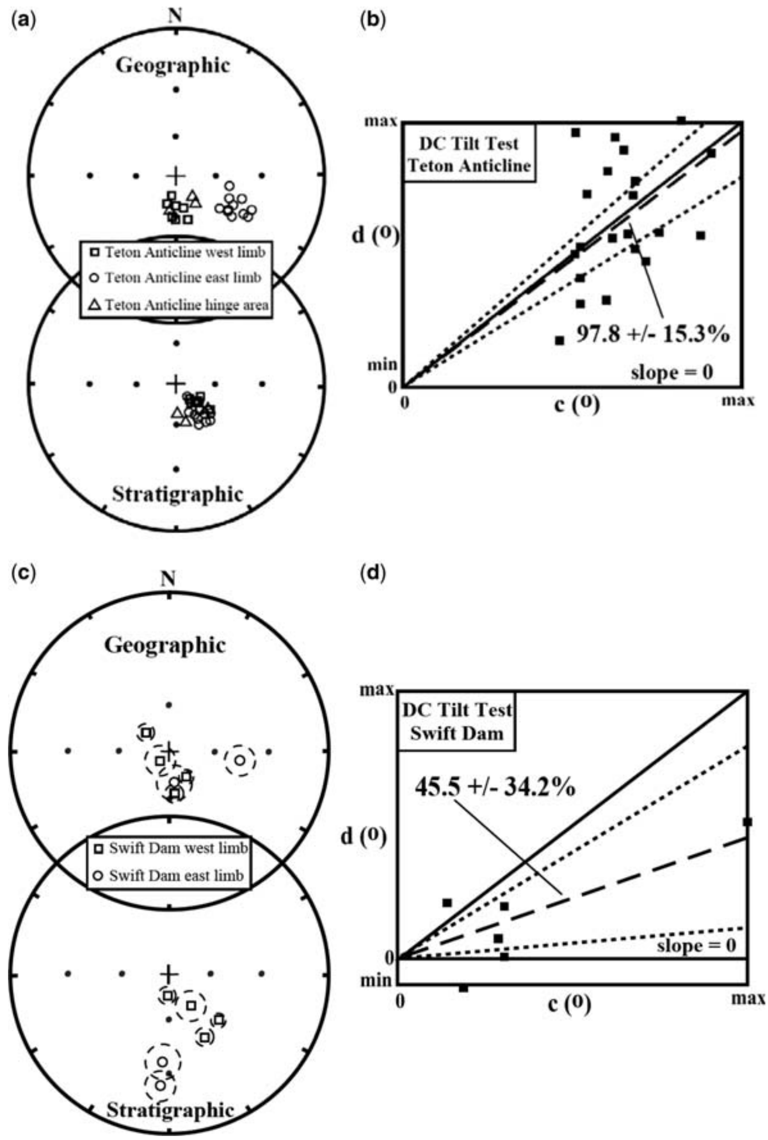


**Fig. 9.** Results from two folds with different geometries in Mississippian rocks in Montana (after O'Brien *et al.* 2007). (**a**) Equal-area projection for the site means of the Teton anticline (fault-bend fold) in geographic (0% untilting) and stratigraphic (100% untilting) coordinates. Circles represent the east limb, squares represent the west limb and triangles represent the hinge area of the fold. The mean $\alpha_{95}$ of the Teton anticline sites is 7.2 (standard deviation of 2.5, $n = 19$). Open circles are negative inclinations. (**b**) DC tilt test results (Enkin 2003). Optimal clustering is not significantly different than 100%, indicating a positive tilt test result. (**c**) Equal area projection for the site means of the Swift Dam fold (fault-propagation fold) in geographic (0% untilting) and stratigraphic (100% untilting) coordinates. Circles represent the east limb and squares represent the west limb on the fold. The dashed circles represent the $\alpha_{95}$ of the site means. (**d**) DC tilt test results. Optimal clustering indicates an indeterminate tilt test result in which there was a syntilting acquisition or an incomplete separation of pre- and post-tilting components.

remagnetization event. Tilt test results however suggest that the CRM is pre-tilting in both the thrust sheets and a fold with a fault-bend fold geometry and syntilting in folds with a fault-propagation fold geometry (Fig. 9) that probably experienced higher strains.

Experimental studies suggest that geologically reasonable differential stress levels can cause the acquisition of a PRM in carbonates (Borradaile 1994) as a result of magnetic domain migration in magnetite (Xu & Merrill 1992; Borradaile & Jackson 1993). A PRM should theoretically require more stress than most rocks have been subjected to during deformation, be partially reversible and have the greatest effect on the low-coercivity phases (e.g. Borradiale 1997).

In summary, the results from some studies suggest that pre-folding CRMs may have been altered into a syntilting configuration, perhaps as a result of strain. Additional studies are needed to further test this hypothesis, however. Although not widely applied in palaeomagnetic studies, optimal differential untilting (Enkin *et al.* 2000; Elmore *et al.* 2006*b*) or small circle intersection (SCI) analysis (Shipunov 1997; Waldhöer & Appel 2006) may help facilitate a better understanding of syntilting remagnetizations.

## Other remagnetization mechanisms

Numerous studies have documented that pyrrhotite can carry a CRM (e.g. Dekkers *et al.* 1989; Rochette *et al.* 1990; Jackson *et al.* 1993; Hirt *et al.* 1995; Xu *et al.* 1998; Weaver *et al.* 2002; Crouzet *et al.* 2003; Gillett & Karlin 2004; Font *et al.* 2006; Preeden *et al.* 2008; Manning & Elmore 2012). Although some of the remagnetizations are thermoviscous in origin (Kligfield & Channell 1981), many are interpreted to be chemical in origin with several remagnetization mechanisms proposed. These include pyrrhotite authigenesis caused by thermochemical sulphate reduction (Pierce *et al.* 1998; Zechmeister *et al.* 2012), migration of hydrocarbons (Machel & Burton 1991) or oxidation of pre-existing pyrite (Salmon *et al.* 1988). Chemical alteration by gas hydrates (Housen & Musgrave 1996; Larrasoaña *et al.* 2007) and pore fluids (Urbat *et al.* 2000) have also been suggested as mechanisms.

Pyrrhotite remagnetization in the Himalaya has been documented in numerous studies during the past 20 years and the reader is referred to Appel *et al.* (2012) for a history of such studies. Some of these remagnetizations are thermoremanences, but in cases where the peak metamorphic temperature ($T_{max}$) is less than the Curie temperature ($T_c \approx 325\ ^\circ C$) the magnetizations can be chemical, thermochemical or thermoremanent in origin (Appel *et al.* 2012).

Remagnetization by cooling during uplift (thermoviscous) is likely for some units that experienced moderate-to-elevated burial temperatures. A thermoviscous mechanism is the best explanation for some magnetizations in the Appalachians (e.g. Kent 1985). Careful attention to thermal histories is necessary when attempting to evaluate the possibility of a thermoviscous remagnetization. Thermoviscous remagnetizations have also been used as geothermometers (e.g. Pullaiah *et al.* 1975; Middleton & Schmidt 1980; Crouzet *et al.* 1999; Dunlop *et al.* 2000).

Recent studies have also presented evidence that greigite ($Fe_3S_4$) can carry a diagenetic magnetization (e.g. Roberts & Weaver 2005; Rowan *et al.* 2009). Roberts & Weaver (2005) describe five mechanisms of CRM acquisition in greigite.

## Rock magnetic characterization of chemical remagnetization

In attempting to develop a better understanding of remagnetization processes and use palaeomagnetism to date diagenetic events, it is of obvious importance to identify the magnetic minerals that are carrying the remanence; rock magnetic studies are crucial in this endeavour. A general overview of this topic is covered in this paper, but the reader is also referred to other papers in this volume by Jackson & Swanson-Hysell (2012) and Dekkers (2012) as well as to previous publications (e.g. Dunlop & Özdemir 1997) for a more detailed discussion.

Although demagnetization characteristics provide some information, rock magnetic studies are needed to fully characterize magnetic mineralogy. Low-temperature demagnetization (LTD) by liquid nitrogen treatment prior to demagnetization has proven successful in removing magnetizations held in multi-domain (MD) magnetite (Dunlop & Argyle 1991). In addition to removing a modern magnetization in magnetite that could contaminate the characteristic magnetization, some specimens that were subjected to LTD also displayed more stable decay on the orthogonal plots than those that were not subject to the treatment (Manning & Elmore 2012).

Standard rock magnetic techniques include isothermal remanent magnetization (IRM) acquisition and thermal decay experiments (Lowrie 1990). As described in Dekkers (2012), end-member modelling of IRM acquisition curves has shown promise in determining the individual coercivity contributions. It is worth noting that these rock magnetic techniques provide information on all the magnetic phases in the rock, not just the minerals that carry the CRM.

The results of previous rock magnetic studies suggest that single-domain magnetite in remagnetized carbonates lacks shape anisotropy and that the magnetic properties are controlled by cubic magnetocrystalline anisotropy; this is consistent with the diagenetic origin for many secondary magnetizations (e.g. Jackson 1990; Jackson & Sun 1992). As pointed out by Jackson & Swanson-Hysell (2012) in this volume, recent studies have demonstrated that the magnetic signature in some units is not controlled by cubic magnetocrystalline anisotropy but by uniaxial anisotropy.

Low-temperature (LT) experiments to identify the 120 K Verwey transition in magnetite (Verwey 1939) and 34 K Besnus transition in pyrrhotite (Rochette *et al.* 2011) have proven useful in identifying magnetite and pyrrhotite in rocks (Dekkers *et al.* 1989; Rochette *et al.* 1990; Manning & Elmore 2012; Zechmeister *et al.* 2012). Hysteresis properties can also be used to identify the magnetic mineralogy and to characterize the type and size of magnetite (single-domain, pseudo-single-domain or multi-domain) in order to make inferences about the remagnetization processes. Many CRMs have wasp-waisted hysteresis loops, which are interpreted to reflect the presence of a range of magnetic grain sizes and/or magnetic minerals (e.g. Jackson 1990; Roberts *et al.* 1995). Determining the hysteresis parameters (including the coercivity of remanence $H_{cr}$, coercive force $H_c$, saturation remanence $M_{rs}$ and saturation magnetization $M_s$) can also be very useful (Tauxe 2005). For example, on a plot of coercivity ($H_{cr}/H_c$) and remanence ($M_{rs}/M_s$) ratios, CRMs commonly have high remanence values compared to the coercivity ratios (e.g. Jackson 1990; McCabe & Channell 1994). This property, along with wasp-waisted hysteresis loops, frequency-dependent susceptibility and high ratios of anhysteretic remanence to saturation remanence, is considered a rock magnetic fingerprint of remagnetization. The reader is referred to the paper by Jackson & Swanson-Hysell (2012) for a discussion of the current status of rock magnetism of remagnetized carbonates.

## Summary and unresolved issues

Considerable progress has been made on understanding remagnetization mechanisms during the last five decades. Chemical remanent magnetizations can be used to date a variety of different diagenetic events. We have also learned to identify remagnetization using both rock magnetic and palaeomagnetic data. Despite the progress, a number of important issues related to remagnetization remain to be resolved and warrant further study. Continued integration of magnetic data with diagenetic formation from geochemical and petrographic studies could help resolve many of the issues. Unresolved issues include the following.

(1) Why are many remagnetizations of one polarity? Although palaeomagnetists are finding more dual-polarity CRMs, many CRMS are of one polarity and were acquired during the Late Palzeozoic–Cretaceous long-polarity intervals.

(2) What are the origins of syntilting CRMs? Although many CRMs are syntilting in character, the suspicion exists that some CRMs are not truly syntilting but are instead a result of modification of a pre-folding CRM. Possible explanations include modification of a pre-folding component by contamination or strain, and more research is warranted on this issue.

(3) What is the chemical origin of the widespread Late Palaeozoic CRMs in many Early and Middle Palaeozoic red bed units in the Appalachians? The timing contrasts with other red beds where the haematite is acquired relatively early. One popular model relates these CRMs to the migration of orogenic fluids (e.g. McCabe & Elmore 1989). Little geochemical or petrographic evidence which indicates that the rocks were altered by orogenic-type fluids has been presented.

(4) The principal working hypothesis of the palaeomagnetic dating approach is that diagenetic processes can trigger the authigenesis of magnetic mineral phases and acquisition of a CRM. Geochemical and petrographic studies as well as field tests (vein or contact tests) provide important evidence for establishing these relationships. Additional tests of this hypothesis using independent dating methods to verify the palaeomagnetic ages would be useful.

(5) There is empirical evidence that hydrocarbons can cause significant changes in the magnetic characteristics as well as remagnetization in a number of different rock types. The mechanisms are not understood, however. More research is needed to fully develop the use of magnetic studies in hydrocarbon exploration.

(6) Although there is a significant body of literature on the role of bacteria in causing mineral authigenesis, this area warrants further research.

(7) Although it is clear that LTD can remove low-coercivity unstable secondary components which contaminate a characteristic remanent magnetization, the procedure is not being universally applied. More research on which rocks should be subjected to LTD would be useful.

(8) Although not necessarily directly related to acquisition of CRMs, the effect of inclination shallowing on pole positions used to determine APWPs is necessary if remagnetizations are to be used to date events. For example, Bilardello & Kodama (2010) presented evidence that a correction for

inclination shallowing could cause the Late Palaeozoic APWP to shift to a lower latitude by 4–10°.

(9) Many sedimentary rocks in the Appalachians and other areas contain intermediate-temperature components (unblocking temperatures of 300–350 °C) that are commonly interpreted as thermoviscous remanent magnetizations (TVRMs) in magnetite. Some studies suggest that some of these magnetizations could be CRMs in pyrrhotite. Additional rock magnetic studies could determine the origin of these remagnetizations.

(10) Additional palaeomagnetic and geochemical/petrographic studies of alteration below palaeoweathering surfaces can provide data on the extent of the event and age constraints on the surfaces which are commonly difficult to obtain. This can be useful information to evaluate the evolution (e.g. erosion rates) of ancient continents.

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