Upper Mississippi Valley and Sweetwater Mississippi Valley-type districts, United States of America: Timing of mineralization and dolomitization from paleomagnetism (Tennessee).

Shanmugam Johari. Pannalal

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to form MVT ore deposits in the orogen or adjacent to it. The well-constrained paleomagnetic ages for the two MVT districts further shows the paleomagnetic method to be an efficient tool for defining the timing of fluid flow events that cause dolomitization and MVT mineralization in carbonate host rocks.
CO-AUTHORSHIP STATEMENT

The following thesis contains material from two manuscripts that have been submitted to the Journal of Applied Geophysics and the Journal of Geochemical Exploration.

1. Journal of Applied Geophysics

The manuscript titled, "Paleomagnetic dating of Upper Mississippi Valley zinc-lead mineralisation, Wisconsin, U.S.A.", is co-authored by S.J. Pannalal, D.T.A. Symons, and D.F. Sangster, formerly of the Geological Survey of Canada and now a private consultant in North Gower, Ontario, Canada. The sample collecting was done by D.T.A. Symons and D.F. Sangster. Laboratory work and data analysis presented in this thesis was performed by the author. The submitted version of this manuscript appears in Chapter 2.

2. Journal of Geochemical Exploration

The manuscript titled, "Sweetwater Ba-F-Zn district, eastern Tennessee: a paleomagnetic age for dolomitisation from fluid flow", is co-authored by S.J. Pannalal, D.T.A. Symons and Kula C. Misra. Fieldwork was shared by D.T.A. Symons and Kula C. Misra, Professor, Geological Sciences, University of Tennessee, Knoxville, Tennessee, U.S.A. Laboratory work and data analysis presented in this thesis was performed by the author. The submitted version of this manuscript appears in Chapter 3.
For my parents Meera and Pannalal Johari

With Love
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This thesis is for you, mom and dad.
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LIST OF NOMENCLATURE

AF - Alternating Field
Am\(^{-1}\) - Amperes per metre
APWP - Apparent polar wander path
Ar - Argon
Ba - Barium
BB - Barren belt
Br - Bromine
CAI - Colour alteration index
CB - Central belt
ChRM - Characteristic remanent magnetization
Cl - Chlorine
CRM - Chemical remanent magnetization
Dec - Declination
DRM - Detrital remanent magnetization
EB - Eastern belt
F - Fluorine
GAD - Geocentric axial dipole
Inc - Inclination
k - Precision parameter
K - Potassium
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<tr>
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<tr>
<td>Km</td>
<td>Kilometre</td>
</tr>
<tr>
<td>m</td>
<td>Metre</td>
</tr>
<tr>
<td>M</td>
<td>Mean</td>
</tr>
<tr>
<td>Ma</td>
<td>Million years</td>
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<tr>
<td>MAD</td>
<td>Maximum angular deviation</td>
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<tr>
<td>MD</td>
<td>Multidomain</td>
</tr>
<tr>
<td>mT</td>
<td>Millitesla</td>
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<tr>
<td>MVT</td>
<td>Mississippi Valley-type</td>
</tr>
<tr>
<td>NRM</td>
<td>Natural remanent magnetization</td>
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<tr>
<td>nT</td>
<td>Nanotesla</td>
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<tr>
<td>Pb</td>
<td>Lead</td>
</tr>
<tr>
<td>PCA</td>
<td>Principal component analysis</td>
</tr>
<tr>
<td>PSD</td>
<td>Pseudosingle domain</td>
</tr>
<tr>
<td>Q1</td>
<td>First quartile</td>
</tr>
<tr>
<td>Q3</td>
<td>Third quartile</td>
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<tr>
<td>Rb</td>
<td>Rubidium</td>
</tr>
<tr>
<td>SIRM</td>
<td>Saturation isothermal remanent magnetization</td>
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<td>SD</td>
<td>Single domain</td>
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<td>Sr</td>
<td>Strontium</td>
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<td>Th</td>
<td>Thorium</td>
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<tr>
<td>U</td>
<td>Uranium</td>
</tr>
<tr>
<td>UMV</td>
<td>Upper Mississippi Valley</td>
</tr>
<tr>
<td>VRM</td>
<td>Viscous remanent magnetization</td>
</tr>
<tr>
<td>WB</td>
<td>-</td>
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<td>--------</td>
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CHAPTER 1
MVT ORE DEPOSITS AND PALEOMAGNETISM - A REVIEW.

1.1 MVT ore deposits

Mississippi Valley-type (MVT) ore deposits are stratabound and vein-fill epigenetic ores that include chiefly sphalerite and galena associated with calcite, quartz, dolomite, fluorite or barite. Leach and Sangster (1993) broadly defined MVT lead-zinc deposits as a "varied family" of epigenetic ores precipitated from dense basinal brines at temperatures ranging between 75° and 200°C, typically in platform carbonate sequences and lacking genetic affinities to igneous activity. The name MVT stems from the occurrence of the large, type deposits in the Mississippi Valley basin of North America. MVT deposits occur world-wide as large districts covering hundreds to thousands of square kilometres resulting from massive or partial replacement of carbonates and open space filling of collapse breccia zones or fractures.

As Sangster (1986) stated "other than the general definition of MVT deposits given here, a single descriptive or genetic model for all MVT deposits is an unreasonable expectation", and the great diversity among MVT lead-zinc districts is expected because of the wide range in fluid compositions, geological and geochemical conditions, fluid pathways, and precipitation mechanisms possible at the scale of MVT fluid migration (Leach et al., 2001). However, there is a usage of district names like "Irish-type", "Alpine-type", "Polish-type", "Appalachian-type", etc., for different MVT districts. Also, vein-related fluorite-barite deposits are considered
to be a genetic subtype or variant of typical MVT lead-zinc deposits (Leach and Sangster, 1993). A very detailed summary of Mississippi Valley-type ore deposits has been provided by Leach et al. (2001).

1.2 Dating MVTs?

The main obstacle to understanding the origin of MVT ore deposits has been the enigma behind the timing of ore formation. Advances in the applications of radiometric dating and high precision paleomagnetic techniques during the last decade have considerably improved our understanding on MVT ore genesis. A broad agreement is noted between age dates that have been obtained for MVT deposits by radiometric and paleomagnetic dating techniques. Leach et al. (2001, Table 1) summarize the results of MVT dating studies using paleomagnetic dating or radiometric dating by U-Pb, U-Th calcite, Rb-Sr sphalerite, $^{40}$Ar-$^{39}$Ar or K-Ar on feldspar and clay minerals, and fission track methods. However, radiometric dating of MVT ore deposits has proven difficult because their constituent minerals contain very low concentrations of the radioactive isotopes useful for geochronology (Symons et al., 1996; Leach et al., 2001) resulting in measurement imprecision. Also, contamination by minute traces of exotic materials, such as colloidal clay particles, can cause some serious problems (Brannon, 1995).

Early attempts at dating MVT deposits using paleomagnetism (eg. Beales et al., 1974; Wu and Beales, 1981) were unsuccessful because of the lack of a well-defined apparent polar wander path (APWP) for the Phanerozoic and sufficiently
sensitive measuring equipment. With a well-defined APWP now available and the advent of sensitive, modern, cryogenic magnetometers, the paleomagnetic technique has proven successful in dating MVT deposits. The paleomagnetic dating methodology has been discussed in detail by Symons et al. (1996).

In addition to the timing of ore formation, information on the duration of MVT mineralization is essential to better understand the mineralizing fluid systems. Where radiometric studies provide the age of deposition for a single stage of the paragenetic sequence, paleomagnetic methods record all of the main mineralization stages of the MVT hydrothermal event (Leach et al., 2001). Rowan and Goldhaber (1996), based on fluid inclusion data together with thermal alteration of biomarkers, argued that the ore-forming event in the Upper Mississippi Valley (UMV) district lasted between 37,000 yrs to 1.4 Ma, depending on whether the highest or lowest fluid inclusion homogenization temperatures were used for the calculations. Lewchuk and Symons (1995) and Symons and Stratakos (2002), observed that pre-ore dolomitization in some districts occurred approximately 20 ± 10 Ma prior to mineralization in some MVT districts, based on paleomagnetic evidence. This contrast between the paleomagnetic and thermal alteration techniques, as speculated by Leach et al. (2001), suggests that paleomagnetic studies may yield dates that reflect the life of the regional hydrological system whereas the thermal alteration of organic matter reflects the duration or more time-restricted thermal-pulse within a regional hydrological event.

Also, the question of how MVT deposits formed has been studied at large and argued by geologists for a century and a half (eg. Crook, 1933; Moore, 1939;
Ohle, 1959; Ohle, 1980). Although there is much debate as to the fluid-flow systems responsible for MVT ore mineralization, the recent age dates strongly support a genetic connection between the formation of MVT lead-zinc deposits and large-scale tectonic events in the surrounding or adjacent orogens (Symons et al., 1996; Leach et al., 2001). Recent investigations on most of the major MVT ore deposits of North America by researchers at the Paleomagnetic Laboratory of Windsor have shown that the remagnetization age of the host rocks and the primary magnetization age of the MVT ore deposits are coeval with the age of major tectonic events in nearby orogenic belts (Fig. 1.1, modified from Lewchuck, 1996). The relationship between district-scale MVT ore deposition and adjacent convergent margin tectonics argues that a large-scale brine migration was responsible for ore deposition (Symons et al., 1996; Leach et al., 2001). Proposed mechanisms for MVT ore genesis include models such as the gravity-driven (Garven, 1985; Bethke, 1986), sediment compaction (Jackson and Beales, 1967; Cathles and Smith, 1983) and tectonic "squeezing" (Oliver, 1986) models.

1.3 The Research Project

The main goal of this thesis research has been to use paleomagnetism to date two MVT ore deposits that did not have a well constrained age for mineralization and to date the dolomitization event that usually predates or is coeval with MVT ore deposition. The two projects include the classic MVT deposits from Upper Mississippi Valley (UMV) zinc-lead district, Wisconsin, and the
Fig. 1.1 Location of the North American MVT ore deposits which have been paleomagnetically dated. The shaded areas are the approximate boundaries of the orogenic belts thought responsible for brine migration and MVT mineralization. MJC - Mascot Jefferson City district, eastern Tennessee; UMV - Upper Mississippi Valley district, Wisconsin (modified from Lewchuk, 1996).
enigmatic Appalachian-type MVT deposits of the Sweetwater Ba-F-Zn district, eastern Tennessee, U.S.A.

The timing of mineralization in the UMV district has been highly debated. Brannon et al. (1992) determined an $^{87}\text{Rb} - ^{86}\text{Sr}$ sphalerite age of 270 ± 4 Ma for the UMV MVT mineralization. However, this dating method has given controversial results in several MVT districts that are not supported by geologic or other direct dating evidence. Hence, the aim of this project has been to define the age of the mineralization and the dolomitization events in the UMV district to compare with the $^{87}\text{Rb} - ^{86}\text{Sr}$ sphalerite age of Brannon et al. (1992).

Project two aimed to define the age of mineralization and dolomitization in the Sweetwater Ba-F-Zn district. The chief mineralization in the district includes barite and fluorite with minor sphalerite, which differentiates this Appalachian-type MVT district from the more typical UMV mineralization in the midcontinent. Project two also aimed to compare the Sweetwater age-date with another Appalachian MVT district of eastern Tennessee, the Mascot-Jefferson City MVT district with a well-defined paleomagnetic age (Symons and Stratakos, 2002) lying in the same thrust belt as the Sweetwater district but ~ 70 kms to the northeast.

The paleomagnetic investigation in both of the above research projects includes defining the magnetization characteristics of the ores and their host rocks, i.e. the magnetic mineralogy and the effective grain-size of the magnetic minerals present in these deposits. Summarizing the age dates for MVT ore deposits that have been dated by radiometric and paleomagnetic techniques, Leach et al. (2001) have observed that, excluding the two MVT districts/deposits in Proterozoic rocks,
the vast majority of MVT lead-zinc ore deposits were formed during two windows in
geologic time that correspond to periods of major orogenic activity. The most
important period of MVT ore formation was Devonian to Late Permian that
corresponds to the assembly of supercontinent of Pangea, and the second period
was during Cretaceous and Early Tertiary that corresponds to the Laramide and
Alpine orogenic cycles. The paleomagnetic ages determined for the two MVT ore
deposits of this study will be compared to the two observed time windows of MVT
mineralization. The ultimate goal of this thesis is to constrain possible genetic
models for ore genesis for each of the two MVT districts and to test the hypothesis
of the documented relationship between the formation of MVT ore deposits and
orogenic events in the surrounding or adjacent orogen (Symons et al., 1996; Leach
et al., 2001).

1.4 The Paleomagnetic Dating Method

The conventional paleomagnetic techniques described in a number of
paleomagnetic text books (e.g. McElhinny and Merrill, 1983; Tarling, 1983; Butler,
1992) were used in this research. The measurement, step demagnetization
techniques and field tests used in both of the research projects are described
separately for each in detail. A brief description of the theory of methods in general
are given here, mostly paraphrased from the paleomagnetic text books.
1.4.1 The Principle

Paleomagnetism is defined as the study of the geomagnetic field recorded in rock magnetizations. A fundamental assumption of paleomagnetism is that the time-averaged geomagnetic field corresponds to that of an axial geocentric dipole. Its use in paleomagnetism is essentially an application of the principle of uniformitarianism. It is known from paleomagnetic measurements that the Earth's magnetic field for the past few million years, when averaged over periods of several thousands of years, has conformed to this model, so that it is then used as a working hypothesis through geological time.

The requirement that the mean paleomagnetic pole position derived for a collection of rocks should represent the axial geocentric dipole is taken into account in the methodology of paleomagnetic analysis. This begins with the sampling of a rock formation on hierarchical scheme designed to eliminate or minimize non-systematic errors and to average out the effects of short-term (<10^4 Ma) secular variation in the geomagnetic field. At each hierarchical level, averaging and statistical analysis are carried out on the remanent magnetization vectors. Most paleomagnetic studies involve the collection and orientation of samples using a sun or Brunton compass, followed by laboratory measurements of their susceptibility and natural remanence; the natural remanence must then be examined for its stability and the possible age(s) of its component(s), thus defining the directions and intensity of the geomagnetic field at some specific time.

MVT mineralization is formed in the host carbonates from hydrothermal fluid flow precipitating new ferromagnetic minerals in the void spaces as inclusions, and
that these ferromagnetic minerals record a primary chemical remanent magnetization (CRM). This CRM represents the geomagnetic field at the time of mineralization which is then isolated by the paleomagnetic method thereby defining the mineralization age. Also the host rocks of the MVT mineralization carry a remanent magnetization that is a CRM and with possibly a minor contribution of detrital remanent magnetization (DRM). The dolomitization of these host carbonates results from the hydrothermal fluid flow event responsible for mineralization and/or with the involvement of burial loading mechanism. The dolomitization of calcite records a chemical remagnetization that is carried chiefly by inclusions of single domain or pseudosingle domain ferromagnetic minerals. Also, with increased pressure and temperature because of burial loading, the very-fine grained calcite or dolomite will recrystallize into larger grains. This process plus the involvement of a hydrothermal fluid causes new ferromagnetic minerals to be formed as inclusions, which then record a chemical remagnetization in the host rocks that defines the geomagnetic field at the time the host carbonates were recrystallized.

1.4.2 The Geocentric Axial Dipole Model

Geocentric axial dipole (GAD) is a concept central to many principles of paleomagnetism. In this model (Fig. 1.2), the Earth's magnetic field is considered to be produced by a single magnetic dipole at the center of the Earth that is, when time averaged, aligned with the rotation axis. The inclination of the field can be determined by
Fig. 1.2 Ideal cross-section of the Earth, illustrating the Geocentric Axial Dipole Model. The observed magnetic inclination, \( I \), between the magnetic vector and local horizontal at any location is a function of magnetic latitude, \( \lambda \), according to the indicated equation (adapted from Butler, 1992).

\[
\tan I = 2 \tan \lambda
\]
\[ \tan I = \frac{H_v}{H_h} = 2 \frac{\sin \lambda}{\cos \lambda} = 2 \tan \lambda \] ............ (a)

where \( H_v \) is the vertical component and \( H_h \) is the horizontal component of the magnetic field, \( H \), respectively; \( \lambda \) is the paleolatitude and \( I \) is the paleoinclination, \( I \), which increases from -90° at the south magnetic pole to +90° at the magnetic north pole. Lines of equal \( I \) are parallel to the lines of paleolatitude and are simply related through Equation (a). It is a cornerstone of the paleomagnetic method and is often referred to as "the dipole equation". This relationship between \( I \) and \( \lambda \) is fundamental and essential to understanding many paleogeographic and tectonic applications, including dating ore deposits using paleomagnetism. For a GAD, declination, \( D = 0° \) everywhere (Butler, 1992).

1.4.3 The Equipment

A very sensitive cryogenic magnetometer is essential for the paleomagnetic dating of MVT deposits. Assuming they are measured inside a magnetically-shielded room with an ambient magnetic field of \( \leq 100 \) nT, most existing cryogenic magnetometers can reliably measure remanence intensities down to \( \sim 5 \times 10^{-6} \text{Am}^{-1} \). Since the desired characteristic remanent magnetization (ChRM) is usually measured in the last 10 - 30 % of the natural remanent magnetization (NRM) after demagnetization, very sensitive magnetometers are required for reliably measuring ChRMs of the MVT deposits where the initial NRM intensities are typically \( \sim 2 \times 10^{-4} \text{Am}^{-1} \). The Windsor paleomagnetic laboratory used to operate a Canadian Thin
Films (CTF) cryogenic magnetometer, modified with computer signal stacking and an automated measurement cycle, with an effective sensitivity limit of $\sim 5 \times 10^{-6}$ Am$^{-1}$, enough to yield measurable ChRM data from MVT deposits. This magnetometer was used to measure samples from the Upper Mississippi Valley, the first project in this research.

With the recent developments and installation of new equipment during the fall of 2001, the Windsor paleomagnetic laboratory now operates a 2G Enterprises 755R DC-SQUID superconducting rock magnetometer. It has a 2G800 automated sample handler system with a specially modified rapid measurement cycle that operates in vertical position rather than in the usual horizontal position. With a $\sim 2 \times 10^{-6}$ Am$^{-1}$ sensitivity, this is one of the most sensitive and efficient magnetometers in the world. Also, this magnetometer completes a measurement cycle in $\leq 50$ seconds so that large collections of specimens can be tested. This is important because the confidence limit on a remanence direction is dependent on the number of specimen directions averaged and the confidence limit is used to give limits on the age. Thus the larger number of ChRM directions averaged, the smaller the age errors are likely to be (Symons et al., 1996). The specimens from the Sweetwater Ba-F-Zn district of eastern Tennessee, were measured using the 2G magnetometer.

1.4.4 Sampling

The paleomagnetic sampling involves collection of oriented samples from suitable rock exposures which are in situ. Unlike radiometric age dating in which a few milligrams of ore-stage mineralization is dated, paleomagnetic dating entails
sampling several kilograms of material from an ore body at many different places. Samples are collected either by hand sampling oriented blocks or by drilling cores from an outcrop using a portable rock drill, following the generalized paleomagnetic sampling scheme (Fig. 1.3, Butler, 1992).

Ideally, about 6 cores (~ 8 to 10 cores or hand-sampled blocks for breccia/conglomerate and fold tests) are drilled at a site and sampling is done at ~ 20 - 30 sites in a given geologic unit to define the mean ChRM direction for each site and the mean ChRM direction for the unit. The individual samples (cores) thus collected are cut into right-cylindrical specimens of standard size (2.54 cm diameter by 2.20 cm height) in the laboratory. The actual shape of a specimen is critical in many measurements, the most common shapes being cubes and cylinders. Once the specimens were prepared, they were stored in a magnetically-shielded room with an ambient magnetic field of ≤ 100 nT for several weeks prior to measurement or experimental analysis in order to permit their acquired unstable viscous remanent magnetization (VRM) to decay substantially.

1.4.5 Experimental Methods

Partial demagnetization techniques are used to 'magnetically clean' the NRM so that the component of the NRM can be analyzed and the stable components isolated. All the specimens were step demagnetized using alternating field (AF) or thermal demagnetization techniques discussed briefly below. Specimens from outcrops that have been struck by lightning have an intense VRM that must be
<table>
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<td>Sample E</td>
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Fig. 1.3 Generalized paleomagnetic sampling scheme. Multiple sampling sites are collected within the rock unit; multiple samples are collected from each site; specimens for laboratory measurements are prepared from samples (adapted from Butler, 1992).
removed by one of the cleaning techniques. The two main step-demagnetization methods used in this research are briefly discussed here.

(a) Alternating Field (AF) demagnetization

The fundamental demagnetization procedure is to expose a specimen to an AF field. When a rock sample is placed in an alternating magnetic field, the grain magnetic moments with coercivities less than the peak value of the field are weakly remagnetized in random directions as the intensity of the AF is reduced slowly and uniformly to zero; the field cannot affect a magnetization component with coercivity higher than the peak field. The part of the remanence that remains after a demagnetization treatment has been 'magnetically cleaned'. The demagnetization procedure is repeated using successively higher values of the peak field, remeasuring the remaining magnetization after each step, until the magnetization is reduced to zero. The effectiveness of the AF demagnetization method is limited by the strongest peak field that can be produced in the demagnetizing coil, the stability of the magnetic mineral, and the quality of the magnetic field free space in which the demagnetization is done.

AF demagnetization is often effective in removing secondary remanence components and isolating the ChRM in rocks with titanomagnetite as the dominant ferromagnetic mineral. The unwanted VRM found in the MVT ores and their host rocks is routinely present in AF fields up to ~30 mT. More significant is that AF cleaning up to 130 mT is commonly required to effectively isolate the ChRM, particularly if pyrrhotite is present. A problem occurs when specimens are collected
from open pits or outcrops because they may contain goethite as a result of weathering. The goethite's recent remanence may be removed by an initial 140°C thermal demagnetization step (Dekkers, 1990; Symons et al., 1996) before AF demagnetization is used to isolate the ChRM in magnetite. In this study the specimens were AF demagnetized using a Sapphire instruments (SI-4) AF demagnetizer.

(b) Thermal demagnetization

An alternate method of 'magnetic cleaning' is progressive thermal demagnetization. The procedure for thermal demagnetization involves heating a specimen to an elevated temperature below the Curie temperature of the constituent ferromagnetic minerals, then cooling to room temperature in zero magnetic field. In stepwise thermal demagnetization, the heating and cooling cycle is repeated with progressively higher maximum temperatures. The progressive randomization of the lower blocking temperature magnetization reveals the residual higher temperature components present in the specimen's NRM. Thermal demagnetization is best suited for removal of VRM in rocks where goethite or hematite is a significant ferromagnetic mineral. Thermal demagnetization of specimens in this study was performed using a Magnetic Measurements MMTD-80 thermal demagnetizer. The major problem with the method for MVT specimens is that iron-bearing sulphides oxidize to form new magnetic minerals, beginning at \( \sim 400^\circ \text{C}, \) so that the method is not effective for a magnetic ChRM when these sulphides are present.
1.4.6 Field Tests

Laboratory demagnetization experiments reveal the constituent magnetic components of the NRM and allow a definition of the ChRM. Blocking temperature and/or coercivity spectra suggest whether or not the ferromagnetic grains carrying a ChRM are capable of retaining a primary NRM. Field tests of paleomagnetic remanence stability can provide crucial information about the timing of ChRM acquisition. Common field tests of paleomagnetic stability include the fold test (or bedding-tilt test), the conglomerate test, the baked contact test and the various consistency tests (Fig. 1.4). A detailed description of the paleomagnetic field tests are provided in a number of paleomagnetic text books (e.g. Tarling, 1983; Butler, 1992).

In the Sweetwater study oriented samples or blocks were collected from sites with sufficiently appreciable difference in bedding attitudes for fold tests. Also breccia clasts were collected from a few sites for breccia tests. A fold test is useful for deducing the relationship between the timing of ChRM acquisition and of folding, based on the change in the precision parameter (k) of Fisher (1953) before and after tilt correction. The ChRM postdates folding if the ChRM directions are grouped with a high k value before tilt correction and, conversely, if the ChRM directions are well-grouped with a high k value after tilt correction, then the ChRM predates folding. The fold test of McElhinny (1964) was used in this study. The breccia test is useful in deducing if the ChRM acquisition occurred before or after the formation of the breccia. If the clast ChRM directions are clustered then the rock was remagnetized after brecciation and if they are randomly oriented then the rock was
Fig. 1.4 (A) Schematic illustration of the fold and conglomerate tests of paleomagnetic stability. Long arrows are directions of ChRM in limbs of the fold and short arrows in cobbles of the conglomerate; random distribution of ChRM directions from cobbles to cobbles within the conglomerate indicates that ChRM was acquired prior to the formation of the conglomerate; improved grouping of ChRM upon restoring the limbs of the fold to the horizontal indicates ChRM formation prior to folding. (B) Directions of ChRM are shown by arrows for prefolding magnetization. ChRM directions are dispersed in the observed in situ orientation; restoring bedding to horizontal results in maximum grouping of the ChRM directions. (C) Directions of ChRM for Synfolding magnetization. ChRM directions are dispersed in both the in situ orientation and when bedding is restored to horizontal; maximum grouping of the ChRM directions occurs when bedding is partially restored to horizontal (adapted from Butler, 1992).
not been remagnetized after brecciation. The breccia test of Graham (1949) was used in this study.

1.4.7 Rock Magnetics

The magnetic mineral carriers of the stable ChRM components were studied using saturation isothermal remanence (SIRM) tests. This method is helpful in characterizing the magnetic mineralogy and its effective grain size in a specimen. SIRM methods were used because AF demagnetized specimens can be further utilized, because the experiment can be done easily and rapidly, and because only a relatively inexpensive pulse magnetizer is needed as additional equipment. SIRM analyses were done using a Sapphire Instruments (SI-6) pulse magnetizer on a suite of specimens that represent the various lithologies present to better characterize their magnetic remanence carriers and magnetic grain size. The process involves pulse magnetizing the specimens in D.C. fields up to 900 mT and then demagnetizing them in AF fields up to 140 mT. A method of plotting the SIRM data has been discussed in detail by Symons and Cioppa (2000).

1.4.8 Statistical Analysis

Following partial demagnetization, ChRM directions were obtained using the least-squares principal-component analysis (PCA) method of Kirschvink (1980). For weakly magnetized rocks or for rocks in which the ChRM is a small percentage of the total NRM, the ChRM direction vectors from step demagnetization usually follow
a linear trajectory of decreasing intensity with scatter. PCA is a quantitative technique for defining the ChRM direction by determining the best-fit line through the scattered directions of the decaying remanence vectors. In the following studies the ChRM directions were isolated with the requirement of the maximum angular deviation (MAD) angle to be less than 10° and 15°. Once the ChRM direction in each specimen was determined, site and unit mean directions were calculated using Fisher (1953) statistics. The unit mean direction and its dispersion were then used to calculate the pole position and its oval of 95% confidence, and it was compared to the apparent polar wander path (APWP) for North America, to estimate the age of the fluid-flow dolomitizing and mineralizing event. The APWP for North America of Van der Voo (1993) was used in this study which has 2σ error limits on the path. The maximum and the minimums of the oval of 95% confidence when plotted about the pole position on the path that gives the age of the fluid-flow dolomitizing and mineralizing event with its 2σ limits.

1.5 References


Moore, R.C., 1939. Significance of the stratigraphic distribution of Mississippi Valley ore deposits. In: E.S. Bastin (Editor), Contributions to a knowledge of the lead and zinc deposits of the Mississippi Valley region. Geological Society of America Special Paper, pp. 29-38.


CHAPTER 2

PALEOMAGNETIC DATING OF UPPER MISSISSIPPI VALLEY ZINC - LEAD MINERALIZATION, WISCONSIN, U.S.A.¹

2.1 Introduction

The Upper Mississippi Valley (UMV) zinc-lead district is one of the classic Mississippi Valley-type (MVT) ore districts of North America. First mined in the early 1700's, it was a major source of lead and zinc during the latter half of the 1800's and first half of the 1900's, and continued to produce until the 1980's (Heyl et al., 1973; Heyl, 1983). Over the years there has been much speculation about the timing of the UMV mineralization. For example, Heyl et al. (1973) related it to deformation associated with formation of the Wisconsin arch during the late Paleozoic or Mesozoic, and McGinnis (1968) related it to Pleistocene glaciation. Over the past two decades genetic theories for the UMV MVT deposits have been tied to hydrogeological fluid flow models with the ore-forming fluids being derived from a variety of basins or orogens, or both, at differing times (Bethke, 1986; Garven et al., 1993; Rowan and Goldhaber, 1996; Chen et al., 2001; Rowan and de Marsily, 2001).

¹ A version of this chapter has been submitted to the Journal of Applied Geophysics as:

Substantial advances have been made in understanding the origin of MVT deposits over the past dozen years from the application of radiometric and paleomagnetic techniques to directly date the ore minerals (Leach et al., 2001). Although the UMV district has been directly dated by Brannon et al. (1992) at 270 ± 4 Ma using the \(^{87}\text{Rb}-^{86}\text{Sr}\) sphalerite method, this paleomagnetic study was undertaken to date dolomitization and MVT mineralization in the UMV, not only because it is one of the last major MVT districts in North America to be studied paleomagnetically but also to confirm the \(^{87}\text{Rb}-^{86}\text{Sr}\) age given by Brannon et al. (1992).

2.2 Geology

Heyl and co-workers have published numerous descriptions of the geology and mineralization in the UMV district and the following has been mostly paraphrased from Heyl (1983).

The UMV zinc-lead district lies to the west of the northward-trending Wisconsin arch (Fig. 2.1) in Paleozoic sedimentary rocks that lap onto the North American Precambrian Shield about 150 km to the north. South of the Wisconsin arch, the intra-cratonic Illinois basin is separated from the Forest City basin by the Mississippi River arch to the west and from the Michigan basin by the Kankakee arch to the north-east. The UMV district is located at the northern fringe of the Illinois basin where a gentle structural high is defined by the Wisconsin, Kankakee and Mississippi River arches (Buschbach and Kolata, 1991).

The UMV zinc-lead mineralization resides in Cambrian to Silurian strata that
Fig. 2.1 Location of the Upper Mississippi Valley zinc-lead district and its area of outlying minor Mississippi Valley-type mineralization, Central United States, modified from Rowan and Goldhaber (1996).
rest unconformably on the ~1.3 Ga Precambrian basement (Fig. 2.2). The basal Upper Cambrian Mount Simon sandstone is overlain by the Eau Claire, Galesville, Franconia and Trempealeau sandstone formations that are, in turn, overlain by an Ordovician and Silurian platform carbonate sequence. The Franconia sandstones are the oldest exposed rocks, and the Maquoketa shale and Lower/Middle Silurian dolomite formations cap some high hills (Grant and Burchard, 1907; cited in Heyl et al., 1973). The basal Cambrian and the Ordovician St. Peter sandstones underlie the ore zones in the UMV district and represent probable aquifers for regional fluid flow (Rowan and Goldhaber, 1996).

The Paleozoic sedimentary formations strike N 85° W throughout the most of the district, swinging to N 45° W in the western part (Heyl et al., 1959; Heyl, 1968; Heyl et al., 1973; Heyl, 1983). The regional dip is about 1° towards the south-southwest. The strata are folded into low broad undulations that generally trend east-west with dips of less than ~ 3°. Rarely have dips in excess of 15° been observed. Minor faults are common, and a well-developed vertical and inclined joint system prevails throughout the area.

The UMV zinc - lead district covers nearly 8000 km² in northwest Illinois, southwest Wisconsin and east Iowa (Fig. 2.1), and uneconomic mineralization occurs over a surrounding area of 100,000 km² (Heyl and West, 1982). Nearly all known commercial mineral deposits have been in the Galena, Decorah and Platteville formations (Fig. 2.2). Deposits in the St. Peter sandstone lie directly below large sulphide deposits in the overlying formations but were considered subeconomic. Mineralization is found as open-space fillings, in solution and collapse
<table>
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<td>Disconformity</td>
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<td>Decorah</td>
<td>Dolomite, with limestone &amp; shale</td>
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<td>Limestone, with dolomite &amp; shale</td>
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<td></td>
<td>St. Peter</td>
<td>Sandstone, coarse</td>
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***MVT ore - bearing formation

Fig. 2.2 Stratigraphy of the Upper Mississippi Valley zinc-lead district, modified from Heyl et al. (1983).
breccias, pitches and flats, veins, joints and vugs. Zinc-dominant ore bodies are linear or elliptical in shape and occurs as veins and replacements along small reverse and bedding-plane faults associated with structures that have been interpreted to be intermediate to small scale synclinal folds (Heyl et al., 1955; Heyl et al., 1959; Arnold et al., 1996). Lead-dominant ore bodies occur mostly as vertical veins or open space filling in vertical fractures within the Galena Formation. Smaller ore bodies tend to be more randomly distributed and independent of identified structural controls. Small sulphide deposits have been found in the Hopkinton and Edgewood formations; thus mineralization must postdate the Middle Silurian (Fig. 2.2). Regional tectonic deformation predated ore deposition, and ceased by the end of the ore deposition or shortly thereafter. This deformation event produced the joints, major and minor folds, bedding-plane and reverse-faults, shear faults, and several episodes of brecciation in the ores during their deposition (Heyl et al., 1973).

2.3 Sampling and Measurement

Drill cores were collected from 33 sites in the UMV district (Fig. 2.3). Although it is one of the original zinc-lead mining districts in the United States with hundreds of small mining operations, thorough reclamation since the end of mining in the 1980's restricted sampling to rare outcrop exposures and roadcuts for fully oriented cores and to mineralized blocks from waste piles of known mining operations for cores oriented by inclination only relative to bedding. Sites were located preferentially in highly dolomitized and mineralized units. Site 19 was lost in
Fig. 2.3 Sampling site locations in the Upper Mississippi Valley zinc-lead district.
Fig. 2.3 Sampling site locations in the Upper Mississippi Valley zinc-lead district.
sampling. The 474 prepared specimens were stored in a magnetically shielded room with an ambient magnetic field of < 0.1 % of the Earth's magnetic field for about four months to allow their viscous remanent magnetization (VRM) to decay.

Of the 474 specimens measured to get their natural remanent magnetization (NRM), 359 were used for paleomagnetic analysis (Table 2.1). All subsequent measurements were done in the shielded room.

The remanence measurements were made using an automated Canadian Thin Films DRM-420 two-axis cryogenic magnetometer with a sensitivity of ~ 4.0 x 10^{-6} Am^{-1}. Guided by the NRM data, two pilot specimens were selected for each site for alternating field (AF) and thermal step demagnetization tests using a Sapphire Instruments SI-4 AF demagnetizer and a Magnetic Measurements MMTD-80 thermal demagnetizer, respectively. The pilot specimens were AF demagnetized in 13 steps up to 120 mT and thermally demagnetized in 10 steps up to 500°C. Based on the results from the test specimens, most of the remaining specimens were step demagnetized in five thermal steps from 265° to 335°C in sites where a pyrrhotite remanence was observed and/or in 5 steps from 265° to 420°C for sites where a magnetite remanence was observed. The remaining few specimens were AF demagnetized in 12 steps up to 90 mT, with additional steps up to 140 mT in some cases.

Following step demagnetization, the characteristic remanence (ChRM) directions were obtained for each specimen using the least-squares principal-component analysis method of Kirschvink (1980). These directions were isolated using three or more demagnetization steps that defined a vector with the maximum
Table 2.1 Site Mean Remanence Directions

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Total: 359 - 240

Notes: * - Samples collected from blocks; n, step demagnetized specimens used for analysis; n', specimens used to calculate the mean; Dec., Declination in degrees, Inc., Inclination in degrees; $\alpha_{95}$, radius of cone of 95% confidence in degrees; k, precision parameter of Fisher (1953); Lithology: cls - compact limestone; ffs - fine-grained fossiliferous limestone; ils - lithographic limestone. sc - sucrosic dolostone; sp - sparry dolostone; spm - sparry dolostone with mineralization;
angular deviation angle less than 15°. For most specimens the ChRM direction was anchored to the origin. Site mean and the unit mean directions were calculated following Fisher (1953). The pole position and its oval of 95% confidence were calculated using the unit mean direction and its dispersion. The pole position was then compared to the North American apparent polar wander path (APWP) of Van der Voo (1993) to estimate the ages of the dolomitization and the mineralization event.

Information about the magnetic mineral carrier(s) of the ChRM component was obtained by saturation isothermal remanent magnetization (SIRM) testing of selected specimens that represented the different lithologies in the collection. SIRM testing was done by pulse magnetizing the specimens in 14 direct field steps up to 900 mT using a Sapphire Instruments SI-6 pulse magnetizer, and then AF demagnetizing them in 9 steps up to 150 mT. A useful paleomagnetic fold test was not possible because the beds are nearly flat lying throughout the district.

2.4 Rock Magnetism

2.4.1 Host Rocks

The median NRM intensity of the host rock dolostones and limestones is 1.08E-04 Am⁻¹ (first quartile, Q1: 6.85E-05 Am⁻¹; third quartile, Q3: 1.66E-04 Am⁻¹), typical of NRM intensities found in most MVT districts (Symons and Sangster, 1994). The NRM directions are mostly scattered along a great-circle trend between steeply down to the north, the Earth’s present magnetic field direction, and a south-southeast and equatorial direction.
AF step demagnetization of the specimens showed the removal of a modern VRM that about parallels the present Earth's magnetic field direction up to a cleaning field of c. 20 mT, followed by the removal of the ChRM vector by more intense fields (Fig. 2.4 a,b,c). The ChRM direction is shallowly inclined to the south-southeast and it is usually best isolated in the 25 to 90 mT range (Fig. 2.4 a,b). This ChRM direction defines a reverse polarity for the Earth's magnetic field. A few specimens with the same demagnetization pattern were found to have an antiparallel north-northeast and shallow ChRM or normal polarity direction (Fig. 2.4 c). The majority of the specimens decay towards the origin of a component plot on AF step demagnetization except for a few specimens that may have an underlying very stable magnetization in goethite or hematite (Fig. 2.4 b).

Thermal step demagnetization showed the initial removal of a modern VRM up to about 265°C and the isolation of the ChRM at higher temperatures in most specimens (Fig. 2.5 a,b,c). Except for a few, these specimens showed unblocking of the ChRM between 265° and 320°C that is indicative of pyrrhotite. The remanence of the pyrrhotite-bearing specimens becomes moderately to very erratic in direction above 335°C, however a few specimens retain the ChRM direction up to 420°C (Fig. 2.5 a,b), indicating the presence of magnetite. A few specimens without pyrrhotite carry a magnetite ChRM that is unblocked in the 500° - 580°C range (Fig. 2.5 c). Thermal step demagnetization also isolates both a reversed and normal polarity ChRM as noticed in AF step demagnetized specimens. There is no evidence of the removal of a goethite remanence in its diagnostic 80° - 120°C unblocking temperature range. Thus the very stable remanence remaining after AF
Fig. 2.4 Orthogonal AF step demagnetization plots for example specimens of: limestone from (a) site 18 and (b) site 04 with a reversed polarity remanence and dolostone from (c) site 27 with a normal polarity remanence. Note the unresolved residual component in (c) that prevents decay to the origin of the plot. The axes are north (N), east (E), south (S), west (W), up (U) and down (D) with points in the horizontal and vertical planes denoted by circles and triangles, respectively. The axial values are proportionate to the NRM intensity. The labelled steps are in milliTesla (mT).
Fig. 2.5 Orthogonal thermal step demagnetization plots for examples specimens of: limestone from (a) site 18 and (b) site 04 with a reversed polarity remanence and dolostone from (c) site 20 with a normal polarity remanence. Conventions as in Fig. 2.4, except the labelled steps are in degree celsius (°C).
or thermal step demagnetization in some specimens is carried by hematite. The hematite remanence could be of geological origin or produced by oxidation on heating in the oven. The majority of the ChRMs isolated from the host rock dolostone and limestone specimens have an intensity of \( \leq 0.40 \times 10^{-5} \text{ Am}^{-1} \).

The SIRM data for the host rock specimens were examined on cross-over plots (Symons and Cioppa, 2000). The SIRM acquisition and the intensity decay curves for the limestone specimens plot within pseudosingle (PSD) and multidomain (MD) ranges of pyrrhotite, except for a specimen from site 03 which follows the fine-grained hematite curve (Fig. 2.6 a). One of the five tested limestone specimens shows an SIRM acquisition with a rapid increase in intensity to 300 mT with a slower continuous rise thereafter. This pattern indicates that the limestone contains PSD to MD pyrrhotite with a minute percentage of fine-grained hematite. The dolostones behave similarly to the limestones except that their measured values plot within the single domain (SD) to PSD ranges for pyrrhotite (Fig. 2.6 b). Five of the nine SIRM tested dolostone specimens track along or within the PSD pyrrhotite range initially and then migrate across and follow the PSD or coarse-grained hematite curve (Fig. 2.6 b, 1,2,3,4,5). The occurrence of magnetite is not clearly defined by the SIRM curves because the SD magnetite field overlaps the PSD pyrrhotite field. Overall, SD to PSD pyrrhotite is clearly the dominant ChRM carrier with minor hematite and magnetite. Further, the crossover points of the intensity acquisition and decay curves plot are on or near the line where the measured to saturation remanence ratio (\( J/J_{900} \)) is 0.50. This indicates that the pyrrhotite crystals are sufficiently widely dispersed throughout the specimens that their magnetization do not significantly
Fig. 2.6 SIRM acquisition and demagnetization cross-over plots for (a) limestone and (b) dolostone specimens shown as solid lines. J/J_{900} is the ratio of the measured to SIRM intensity at 900 mT. H is the magnetic field intensity in milliTesla (mT). Dashed and dotted lines represent the type curves for single (SD), pseudosingle (PSD) and multidomain (MD) pyrrhotite and hematite respectively.
interact.

2.4.2 Mineralized Blocks

The mineralized blocks have a median NRM intensity of $2.32 \times 10^{-4}$ Am$^{-1}$ (Q1: $1.7 \times 10^{-4}$ Am$^{-1}$; Q3: $3.08 \times 10^{-4}$ Am$^{-1}$), a greater value than that of the dolostones and limestones. Since the mineralized specimens were sampled from blocks of waste from known mining operations, their true declinations are not known, but they do give true ChRM inclinations relative to horizontal bedding planes. Most block specimens were thermally step demagnetized, showing an initial removal of the VRM and unblocking of the ChRM direction at temperatures between 265°C and 320°C, indicating that pyrrhotite is the dominant remanence carrier. A few specimens were AF step demagnetized that also showed the initial removal of the VRM and isolation of the ChRM in the 25 to 90 mT range. A significant number of the AF step demagnetized specimens showed an unresolved residual component that prevents decay to the origin of a vector component plot, suggesting the presence of a residual very stable magnetization in goethite or hematite. The thermal and AF step demagnetization behaviours of the mineralized blocks were similar to that of the dolostones and limestones, except in that the ChRM intensities of the mineralized specimens are typically about 50% of their NRM intensities.

SIRM testing was done on 12 specimens representing the ten mineralized block sites (Table 2.1). The data obtained were plotted on the cross-over plots (Fig. 2.7). The measured values of the mineralized blocks were segregated into two groups based on their SIRM behaviour. The SIRM acquisition and intensity decay
Fig. 2.7 SIRM acquisition and demagnetization cross-over plots for specimens from mineralized blocks shown as solid lines. (a) Specimens characterized by pyrrhotite i.e. group-A. (a) Altered specimens characterized by hematite i.e. group-B. Conventions as in Fig. 2.6.
curves for group-A track along or within the bounded ranges of PSD to MD pyrrhotite (Fig. 2.7 a), but they also show a slow continuing rise in intensity to saturation above about 200 mT. This behaviour is similar to that noticed in the host rocks in one limestone and several dolostone specimens. The group-B specimens show SIRM acquisition and intensity decay curves that track along PSD pyrrhotite boundary to some extent, and then they migrate towards and track along the fine-grained (F) to coarse-grained (C) hematite curves (Fig. 2.7 b), indicating a significant proportion of fine- to coarse-grained hematite from alteration in these rocks.

2.5 Statistical Analysis & Pole position

When the specimen ChRM directions are grouped by site for the host carbonates, they are well-clustered with a radius for their cones of 95% confidence ($\alpha_{95}$) of $\leq 16.3^\circ$ (table.1; Fisher, 1953). The few normal north-northwesterly ChRM directions were switched in polarity to their antipodal directions for the site-mean calculations. A few specimens were excluded from the mean calculations as they gave aberrant directions (Table 2.1). Site 28 is an outlier in an otherwise well clustered limestone group. Therefore the site 28 data are excluded from its unit mean direction calculation. Site 8 is poorly defined ($\alpha_{95} = 22.2^\circ$) with a steeper inclination than other dolostone sites, suggesting presence of an unresolved remanence component that overlaps the true ChRM, and therefore site 8 was excluded also from further statistical analysis. The unit mean directions were
calculated for the remaining 5 limestone and 16 dolostone sites following Fisher (1953) as both populations show a circular distribution (Table 2.2, Fig. 2.8). The unit mean direction of the limestones found using site mean ChRM directions has a declination (Dec) = 151.6°, inclination (Inc) = -7.3°, radius of 95% confidence ($\alpha_{95}$) = 6.3° and precision parameter (k) = 149.8, and that of the dolostones is of Dec = 154.8°, Inc = -7.6°, $\alpha_{95}$ = 3.5° and k = 112.0. The pole positions were then calculated separately for dolostones and limestones using their unit mean ChRM directions. Thus the pole position for limestones is at 43.5°N, 130.5°E ($\delta_p = 3.2°$, $\delta_m = 6.3°$) and that of the dolostones is at 45.1°N, 126.7°E ($\delta_p = 1.8°$, $\delta_m = 3.5°$), where $\delta_p$ and $\delta_m$ are the semi-minor and semi-major axes of the distribution ellipse.

The pole position of the dolostones plots on the Early Permian portion of the North American APWP of Van der Voo (1993) with its polar ellipse overlapping the Pennsylvanian - Permian boundary of the path (Fig. 2.9). The limestones' pole position plots off the Permian portion of the APWP with its ellipse partly overlapping the dolostones' ellipse. Therefore, the pole positions of the limestones and dolostones show that they carry a magnetic overprint that was acquired during the Early Permian. Comparing the unit mean directions for the limestones and dolostones using the statistical test of McFadden and Lowes (1981) showed with 95% confidence that they share a common mean. This suggests that the secondary magnetizations observed both in the limestones and dolostones may relate to the onset of a single fluid flow event. However, the pole position of the limestones plots off the APWP on a line towards the Ordovician pole position,
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Notes: Abbreviations as in Table 1 except: N, number of site mean directions; °N, degrees north; °E, degrees east; dp, dm, semi-axes of the oval of 95% confidence along and perpendicular to the site-pole great circle.
Fig. 2.8 Site-mean remanent magnetization directions of: (a) limestones (circles); (b) dolostones (triangles); and (c) the limestones and dolostones means compared, plotted on the south-east quadrant of an equal-area stereonet. Down (up) vectors are denoted by solid (open) symbols.
Fig. 2.9 Apparent polar wander path for North America from Van der Voo (1993) and Besse and Courtillot (1991) from: (a) the Paleozoic to present, adapted from Symons and Stratakos (2000); and (b) the Pennsylvanian to Permian portion only with the pole and 95% (2σ) confidence oval for ore-stage dolomitization and mineralization, the pole of the host limestones, and the pole for the 270 ± 4 Ma $^{87}$Rb-$^{86}$Sr age of mineralization (Brannon et al., 1992).
indicating that the limestones likely carry a small percentage (~10%) of residual Ordovician primary remanence. The substantial apparent conversion of the primary remanence in the limestones to the Permian direction likely reflects recrystallization of calcite to a larger grain size because of burial loading and/or the fact that dolomitization of limestone typically increases the remanence intensity by an order of magnitude so that even a small percentage of dolomitization significantly changes the ChRM. Therefore, the limestones were excluded from any further statistical analysis. After scaling the path within the Early Permian bounds, the dolostones' pole provides a direct date of $282 \pm 10$ Ma (based on $2\sigma$ limits) for the UMV host rock dolomitization and related MVT mineralization.

The ChRM paleoinclinations found in the mineralized block specimens cannot be used to define the age of the mineralizing event, as their true ChRM declinations are not known. Also, because the blocks may have been drilled with the bedding overturned, the sign for the inclination values may be positive or negative. For the purpose of analysis, all block inclinations are deemed to be negative because almost all of the fully-oriented dolostone specimens give Kiaman reversed negative inclinations. The mineralized block sites were then divided into two groups based on their SIRM data. The group-B specimens are characterized by a dominant hematitic component, and typically have steeper ChRM inclinations. They show random orientations because their sulphides have been weathered and altered to hematite since being mined and piled on surface, giving a significant randomly directed modern chemical remanent magnetization, so that the mineralization ChRM
cannot be isolated. Group-A specimens are characterized by a dominant pyrrhotite component and show shallow ChRM inclinations. Isolation of the hematite-bearing component in the group-B specimens is not possible because the oxidation of the sulphides on thermal demagnetization above ~ 400°C in the oven creates spurious components and because AF demagnetization cannot remove enough of the low coercivity component in the hematite. Also, comparing the ChRM inclinations of group-A (M = -9.1° ± 4.3° (mean and standard deviation), N = 5) and group-B (M = -25.3° ± 5.1°, N = 5) showed with > 95% confidence that their means are significantly different. Therefore the group-B specimens were excluded from any further statistical analysis.

The site mean inclinations for the group-A specimens were compared next with the site mean inclinations of the dolostones using a simple unpaired two-tailed student t test. The 16 dolostone site mean inclinations (M = -7.9° ± 5.6°) and five mineralized block site mean inclinations (M = -9.1° ± 4.3°) from sites 15, 16, 30, 31, and 32, when compared, showed with > 95% confidence that they can be drawn from one population. This indicates that the mineralized blocks, based on paleoinclination only, retain the same overall mean ChRM direction as the dolostones, implying that the mineralizing event occurred at the same time as the host rocks were being remagnetized.

2.6 Discussion

The $^{87}$Rb-$^{86}$Sr sphalerite technique has a questionable record in dating MVT
deposits. It has given a date of 357 ± 3 Ma for the Lennard Shelf MVT deposits of Australia (Christensen et al., 1995) and this has been confirmed by a $^{238}$U-$^{206}$Pb ore-stage calcite age of 351 ± 15 Ma (Brannon et al., 1996). Also, at Polaris in the Arctic Archipelago of Canada, the paleomagnetic age of 367 ± 7 (Symons and Sangster, 1992; Symons et al., 1996) has been confirmed by a $^{87}$Rb-$^{86}$Sr sphalerite age of 366 ± 15 Ma (Christensen et al., 1996). Elsewhere the $^{87}$Rb-$^{86}$Sr sphalerite method has produced more controversial results. For the MVT deposits of East Tennessee, Nakai et al. (1990; 1993) have reported $^{87}$Rb-$^{86}$Sr sphalerite ages of 377 ± 29 Ma and 347 ± 20 Ma, a range that spans most of the Devonian and Mississippian, that are significantly different at >95% confidence, and that disagree with other radiometric and paleomagnetic ages (Symons and Stratakos, 2002). At Pine Point in northern Canada, the $^{87}$Rb-$^{86}$Sr sphalerite method has given replicate ages of 361 ± 13 Ma and 374 ± 21 Ma (Nakai et al., 1993; J.C. Brannon, pers. comm. in Symons et al., 1996), but they conflict with Late Cretaceous - Paleocene ages or age limits from paleomagnetism, apatite fission track, fluid flow modelling, burial history, etc. (Garven, 1985; Qing and Mountjoy, 1992; Symons et al., 1993; Ravenhurst et al., 1994; Symons et al., 1998). In two instances, the $^{87}$Rb-$^{86}$Sr sphalerite method has given values for the ages of certain MVT deposits but with unacceptably large error limits. These are the 458 ± 150 Ma result for the Austinville MVT deposit in Virginia and the 450 to 300 Ma value for the Daniel's Harbour deposit in Newfoundland (Nakai et al., 1993). In another four instances – the Central Tennessee district, the Viburnum Trend in Missouri, the Nanisivik district in the Arctic Archipelago of Canada, and the Navan Zn-Pb deposit of Ireland – the
method has given scattered and uninterpretable results (Brannon et al., 1996; Christensen et al., 1996; Walshaw and Menuge, 1997). Lastly the $^{87}\text{Rb}^{86}\text{Sr}$ sphalerite method gave an age of 590 ± 80 Ma for the Northern Arkansas MVT ore district that is significantly older than the Ordovician and younger host rocks (Nakai et al., 1993). The reasons for these mixed results are not clear but extremely low amounts of the isotopes are being measured so that minute impurities such as colloidal clay particles from the host rocks in the ore-forming fluids may be a serious problem. Also the isotopic variations in a single crystal of sphalerite can be as extreme as for an entire district (Brannon et al., 1996). Further the systematics of the $^{87}\text{Rb}^{86}\text{Sr}$ sphalerite decay system are not yet well understood (Brannon et al., 1996; Pettke and Diamond, 1996). Nevertheless, the paleomagnetic age of 282 ± 10 Ma confirms the $^{87}\text{Rb}^{86}\text{Sr}$ age of 270±4 Ma for the UMV ore mineralization, and supports the merit of trying to apply the method in other MVT districts.

The Early Permian (282 ± 10 Ma) remagnetization age obtained from the Ordovician host rocks indicates that their ChRM's were reset, an expected consequence of fluid interaction by MVT ore-forming fluids (Leach et al., 2001). Statistically, the ChRM inclinations for the mineralized and dolostone specimens are not significantly different, suggesting that the mineralization and the dolomitization events were about coeval. A chemical remagnetization must account for the secondary magnetizations found in these rocks because there is no evidence that the ChRM in the host rock or ore specimens records a thermal remagnetization event. Sangster et al. (1994) reported a conodont Colour Alteration Index value of 1 for the UMV district, indicating that the host rock temperatures never exceeded
50° to 60°C. Given that the maximum burial depths in the UMV district never exceeded about 2500 m, burial temperatures never exceeded about 60°C. This is consistent with fluid inclusion homogenization temperatures in veins of post-ore calcite that give values in the 40° - 70°C range. In contrast, McLimans (1977) report homogenization temperatures from 92 fluid inclusions in the sphalerite veins. Excluding five anomalously high values of > 165°C that could have been produced by necking down of the inclusions (Rowan and Goldhaber, 1996), they show that the Zn-Pb mineralization was emplaced from fluids with initial temperatures of 135 ± 15°C and final temperatures of 90 ± 15°C, and a median range of 115 ± 30°C. Earlier results from Newhouse (1933), Bailey and Cameron (1951), and Hall and Friedman (1963) from other UMV ore deposits also confirm a 100 ± 25°C fluid temperature. Thus, as Sangster et al. (1994) noted, the hotter ore fluids must have been channelled from greater depths upwards from, or through, the St. Peter sandstone aquifer into the carbonate host rocks by the ore-controlling structures. The 282 ± 10 Ma paleomagnetic age also falls within the Kiaman reversed polarity superchron from c. 316 to 252 Ma (Haq and Van Eysinga, 1998), which is consistent with the reversed polarity ChRM found in almost all of the specimens. The normal polarity ChRM found in few specimens suggests that there was at least one short interval of normal polarity during the Kiaman superchron.

The 282 ± 10 Ma age obtained for the UMV zinc-lead mineralization agrees closely with the $^{87}$Rb-$^{86}$Sr sphalerite age (270 ± 4 Ma) determined by Brannon et al. (1992; 1996). They actually reported isochrons from two deposits that gave 269 ± 4 Ma and 277 ± 20 Ma, which were combined to give 270 ± 4 Ma, but which hint at
a longer period of mineralization than the combined result implies. Also, from fluid flow modelling, combined with fluid inclusion and biomarker thermal data, Rowan and Goldhaber (1996) have set a range of likely durations for mineralization between 37,500 years and 1.4 m.y. The agreement between the radiometric and paleomagnetic ages adds confidence to the validity of both dating methods and confirms a well-defined Early Permian age for the genesis of the UMV zinc-lead district. Noting that the dolomitization is primarily a precursor to ore-stage mineralization whereas sphalerite is central to the ore stage in the paragenetic sequence (Heyl et al., 1973), it is possible that this explains why the paleomagnetic age is a little older than the radiometric age. Lewchuk and Symons (1995) have noted that dolomitization precedes mineralization in most districts by some 1 to 8 m.y. Further, the 282 ± 10 Ma age for dolomitization and mineralization in the UMV corresponds to the Alleghenian/Ouachitan orogeny, illustrating the documented relationship in several districts between the formation of MVT ore deposits and orogenic events in the surrounding or adjacent orogen (Symons et al., 1996; Leach et al., 2001).

There has been considerable speculation about the genesis of mineralization in the UMV zinc-lead district over the years because of the lack of a well-defined dates for the dolomitization and mineralization, leading to several current fluid flow genetic models. Topographically-driven fluid flow models related to convergent margin tectonics are considered to provide the best possible explanation for generating the large-scale brine migrations required to form MVT mineralization in the American midcontinent (Symons et al., 1996; Leach et al., 2001). Most
hydrological models suggest a south-to-north fluid flow out of the Illinois basin and into the UMV district structural high (Bethke, 1986; Garven et al., 1993; Arnold et al., 1996; Rowan and Goldhaber, 1996; Chen et al., 2001). The evidence for northward flow in the UMV district is based on a progressive northward cooling of fluid inclusion temperatures from ~ 130°C in the south to ~ 70°C in the north (Arnold et al., 1996). Northward flow through the Illinois basin is indicated by northward decreasing fluid inclusion temperatures in secondary quartz, from northward decreasing fluorine concentrations in cores from the Hicks dome fluorine "high" in the south (Fig. 2.1), from illite/smectite formation at about 260 Ma in the Mount Simon sandstone, and from the northward increasing δ¹⁸O isotope values of authigenic K-feldspars and quartz overgrowths in the Upper Cambrian Mount Simon sandstone from the 14 ± 1 ‰ to 24 ± 2 ‰ and from 22 ± 2 ‰ to 28 ± 2 ‰, respectively (Duffin et al., 1989; Arnold et al., 1996; Rowan and Goldhaber, 1996; Chen et al., 2001). From hydrologic modelling, Bethke (1986) suggested that gravity-driven groundwater flow through the Illinois basin was initiated by the uplift of the Pascola Arch in post-Early Permian to pre-Late Cretaceous time; this model, however, conflicts with the observed dates for UMV dolomitization and mineralization. From modelling also, Garven et al. (1993) suggested that fluids moved westward from the Appalachian basin and northward from the Arkoma basin through the Illinois basin in response to Alleghenian/Ouachitan orogenesis. This model fits the dolomitization and mineralization age constraints for UMV, as well as for all other major MVT districts in the U.S. midcontinent (Fig. 2.10), and has been followed by Arnold et al.
Fig. 2.10 MVT districts in the midcontinental U.S.A. Note that the older deposits/districts are more distant from the Ouachitan-Appalachian orogenic belt. CM, Central Missouri, 303 ± 17 Ma, paleomagnetism, Symons and Sangster (1991); CT, Central Tennessee, 260 ± 42 Ma, Th-Pb ore-stage calcite, Brannon et al. (1996a); 245 ± 10 Ma, paleomagnetism, Lewchuk and Symons (1996); NA, Northern Arkansas, 265 ± 20 Ma, paleomagnetism, Pan et al. (1990); OLB, Old Lead Belt, 286 ± 20 Ma, paleomagnetism, Wisnioweicki et al. (1983); TS, Tri-State, 251 ± 11 Ma, Th-Pb ore stage calcite, Brannon et al. (1996a); UMV, Upper Mississippi Valley, 270 ± 4 Ma $^{87}$Rb-$^{86}$Sr sphalerite age, Brannon et al. (1992, 1996b); 282 ± 10 Ma, paleomagnetism, this study; VT, Viburnum Trend, southeast Missouri, 273 ± 10 Ma, paleomagnetism, Symons et al. (1998a).

There are thermal concerns yet to be resolved for UMV. One is need for the fluids exiting the Illinois basin at ~ 95°C to be increased to ~ 135°C to match the observed fluid inclusion temperatures on the south side of the UMV district, and possibly a second is an explanation for the occasional 185° to 220°C fluid inclusions found in the UMV. Rowan and Goldhaber (1996) proposed that heat from the intrusion of the ~ 270 Ma Hicks dome and related intrusions could have elevated fluid temperatures in the basin for a sufficient time period of ~ 2 x 10⁵ years for mineralization to occur, however, these intrusions are relatively small and are unlikely to have been able to provide either sufficient heat throughout the basin for the time required for both dolomitization and mineralization to occur throughout the UMV or the high fluid inclusion temperatures in the mineralization. Alternatively Spirakis and Heyl (1996) noted that the UMV district is underlain by a highly radioactive Precambrian granite. They argued that convective circulation of fluids leached lead and zinc from the granite and these fluids migrated up Permian-aged fractures to form the deposits. However, the UMV mineralization is in Ordovician host rocks and maximum deformation in the district would have occurred during Ordovician to Devonian time when most of the ~ 4 km of sediments in the adjacent Illinois and Michigan intracratonic sag basins were deposited (Sleep and Snell, 1976; Sleep et al., 1980). Thus the Spirakis and Heyl (1996) model conflicts with the age dating because the model implies an Ordovician to Devonian age. An alternative scenario is that uplift in the Appalachain-Ouachitan belt provided, for the
first time after the Cambrian, a sufficient hydraulic head to drive fluids upwards into
the UMV district of the Wisconsin arch, thereby driving hot fluids up through the
underlying granites and sandstones into the overlying platform carbonate sequence
along pre-existing fractures. Such a mechanism provides the potential for localized
"hot spots" to explain the high fluid inclusion temperatures if necessary and, by
mixing fluids coming through the granite that carry heat produced by radioactive
decay with fluids coming from the basin through the sandstones, to preferentially
elevate the temperatures along the south side of the UMV district. Also this variant
of the model satisfies the age constraints and it is permissive geochemically with
respect to Cl/Br ratios (Bartos, 2001; Rowan and de Marsily, 2001). Rowan and de
Marsily (2001) suggested that groundwater recharge in the Ouachita mountains to
the south induced gravity-driven fluid flow northwards through aquifers in the
Reelfoot Rift where subaerial evaporites were dissolved to form brines, on through
the Illinois basin and into the UMV district. This routing explains the Cl/Br ratios
found in inclusions which are mid-range for MVT deposits worldwide and close to
the subaerial-submarine evaporite boundary (Rowan and de Marsily, (2001, Fig.5)).
Bartos (2001) has pointed out from the analysis of Michigan basin waters that the
UMV Cl/Br ratios could also be obtained by Appalachian recharge water moving
through the Appalachian and Michigan basins into the UMV district. This model is
further supported by the east to west fluid trend based on Pb$^{206}$/Pb$^{204}$ and Pb$^{208}$/Pb$^{204}$
ratios given for the UMV district by Heyl et. al. (1966).

On a regional scale UMV ore genesis fits into the time pattern being
established for MVT districts in the midcontinental U.S.A. (Fig. 2.10). Those districts
close to the Ouachitan-Alleghenian orogenic deformation front give somewhat younger ages of 245 Ma to 265 Ma for ore genesis, whereas those more distant from the front give ages of 270 to 303 Ma. One proposed explanation that fits this pattern was given by Symons and Sangster (1994) who adopted the deformation model of Quinlan and Beaumont (1984). They pointed out that the foreland bulge of an orogenic front migrates towards the orogenic belt as orogenic deformation occurs. Symons and Sangster (1994) observed that MVT deposits would form preferentially in the foreland bulge because fluid flow would be ponded in the bulge allowing sulphide minerals to precipitate. It is possible also that the foreland bulge would trap hydrocarbons to act as a reducing agent to cause precipitation. This model speculates that the ~ 50 Ma duration of MVT mineralization events in the U.S. midcontinent, that the several million years required to form MVT deposits in a given district that paleomagnetic dating methods imply, and that the differences in ages of MVT districts of comparable distance from the front can be accounted for by tying fluid flow events to varying flow paths and to periods of rapid uplift in the Ouachitan-Alleghenian orogeny. Further, sulphide precipitation progressively closer to the deformation front with time would be favoured during the waning stages of an orogeny as the hydraulic head is reduced by erosion of the highlands.

2.7 Conclusions

The following conclusions are drawn from this paleomagnetic study of the UMV zinc-lead MVT district.
1. The Ordovician host rock limestones and dolostones were remagnetized to acquire their present secondary ChRM directions during the Early Permian. Coincidentally, sparry dolomite with sphalerite and galena mineralization was emplaced both by open space-filling and by replacement with a primary chemical remanent magnetization. Thermal step demagnetization and SIRM analyses show that the primary synmineralization remanence is carried dominantly by inclusions of single-domain to pseudosingle domain pyrrhotite with a minor contribution from magnetite.

2. The paleomagnetic age of 282 ± 10 Ma for the UMV dolomitization and zinc-lead mineralization is consistent with the $^{87}\text{Rb}-^{86}\text{Sr}$ sphalerite mineralization age of 270 ± 4 Ma (Brannon et al., 1992). This is the third MVT district in which the $^{87}\text{Rb}-^{86}\text{Sr}$ sphalerite age has agreed with an independent direct-dating method for mineralization, indicating the utility of the method for dating MVT ores. Also it provides another example for which there has been close agreement between the paleomagnetic and radiometric ages for mineralization in an MVT district (Symons et al., 1996; Leach et al., 2001).

3. The Early Permian age for the UMV mineralization corresponds to the Alleghanian/Ouachitan orogeny and thus it supports genetic models that relate dolomitization and MVT mineralization in the UMV district (e.g., Garven et al., 1993; Arnold et al., 1996; Rowan and Goldhaber, 1996; Chen et al., 2001; Rowan and de Marsily, 2001) and in the U.S. midcontinent as a whole (e.g., Leach and Rowan, 1986; Symons and Sangster, 1991; Symons et al., 1996; Leach et al., 2001) to uplift events in the orogen.
2.8 Acknowledgements
We take pleasure in acknowledging the support of A.V. Heyl (retired), U.S. Geological Survey, who provided advice and directions to suitable sampling localities in the UMV district. The authors also thank P.J.A. McCausland, of the University of Western Ontario for assistance in collecting and sample preparation, Dr. Mike Harris and Dr. Maria Ciooppa of the University of Windsor for the technical help and support provided during this research, and the Natural Sciences and Engineering Research Council of Canada for grant funding to support this research.

2.9 References


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CHAPTER 3

SWEETWATER BA-F-ZN DISTRICT, EASTERN TENNESSEE: A PALEOMAGNETIC AGE FOR DOLOMITIZATION FROM FLUID FLOW

3.1 Introduction

The Sweetwater Ba-F-Zn district of Tennessee is an enigmatic Mississippi Valley-type (MVT) district compared to the Mascot-Jefferson City and Central Tennessee MVT districts of Tennessee because it is known for its residual barite rather than its sphalerite (Fig. 3.1 A). This has led to its omission in earlier reviews of Appalachian (Hoagland, 1976) or eastern Tennessee MVT zinc-lead deposits (Hoagland et al., 1965; Misra et al., 1983; Misra et al., 1989). However, recent exploration by US Borax has shown significant amounts of sphalerite with trace amounts of galena in the carbonate host rocks of the Sweetwater district (Misra et al., 1989). Mining in the district started as early as 1826 and it remains the only major barite district to have been mined other than Cartersville, Georgia, in the Appalachian Valley and Ridge province (Laurence, 1960).

The southern Appalachian Valley and Ridge province is bounded by the Blue Ridge Province to the southeast and Appalachian Plateau to the northwest and

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encompasses most of the Appalachian MVT districts, including Sweetwater (Fig. 3.1A). Deformation of Cambrian to Pennsylvanian carbonates and clastics in the province created a series of NE-SW trending faults during the Alleghenian Orogeny (Hatcher, Jr. and Odom, 1980). Northwest-verging thrusts with displacements of kilometres produced a well defined pattern of parallel low-angle SE-dipping thrust sheets in the Paleozoic strata (Misra et al., 1989) but not in the basement rocks (Rodgers, 1949).

Mineralization in the Sweetwater district is hosted by Lower Ordovician carbonates. The timing of ore-forming event remains debatable because of the wide variability in dates obtained by various methods. For example, $^{40}\text{Ar}/^{39}\text{Ar}$ dating has given an age of 290 ± 20 Ma (Heam et al., 1987), strontium isotopic ratios a maximum age of 460 Ma (Kesler et al., 1988), and paleomagnetism a Late Carboniferous age based on data from 3 sites (Bachtadse et al., 1987). The age of MVT mineralization has been determined for many midcontinental US and other districts worldwide using paleomagnetic dating techniques (Leach et al., 2001). This paper provides paleomagnetic data for the Sweetwater district with the aim of dating its dolomitizing and mineralizing event(s).

3.2 Geology

The stratigraphy and structure of mineralization in the Sweetwater district are well documented by Misra et al. (1989), adding to earlier geologic reviews that speculate on its ore genesis (e.g, Laurence, 1960; Hill and Wedow, 1971; Laurence, 1971). The Lower Cambrian to Middle Ordovician sedimentary strata are nearly
2260 m thick. They strike generally N 30° - 45° E with a dip of 5° - 35° to the southeast. The strata outcrop in several NE-SW-trending belts that are separated by thrust faults. The Sweetwater mineralization is chiefly found in the Western (WB), Central (CB), and Eastern belts (EB). A 'Barren Belt' (BB) between the CB and the EB was previously deemed to be devoid of mineralization, but recent exploration by US Borax has shown it also contains mineralization (Misra et al., 1989). The world-class Mascot-Jefferson City MVT district is ~70 km to the northeast in the same structure as the BB.

The Lower Cambrian Rome Formation, the oldest beds exposed in the district, is overlain by the Conasauga Group. The overlying Knox Group comprises unmineralized Upper Cambrian Copper Ridge Dolomite and Chepultepec Dolomite, and mineralized Lower Ordovician Kingsport Formation and Mascot Dolomite. The Kingsport Formation, composed chiefly of limestones and medium to coarse grained dolostones, and the overlying Mascot Dolomite, composed of very-fine to fine grained dolostones with limestone interbeds and sandstone intercalations, are capped by the post-Knox angular unconformity. Above are unmineralized Middle Ordovician formations. Economic mineralization in the district has included barite, fluorite and sphalerite. They occur chiefly as open space or fracture fillings in breccia bodies along with minor gangue minerals that include dolomite, pyrite, marcasite, galena, calcite, and jasperoidal silica. Fluorite with minor sphalerite is found also as 'bedded' or 'wing' ore zones that extend laterally through limestone units. A 'break through' ore zone that cuts through different stratigraphic units contains barite, fluorite and sphalerite mineralization. Economic barite occurred as
a residuum at the subcrop-overburden interface in response to Late Tertiary chemical weathering as the Appalachian mountains have risen in seeking isostatic equilibrium.

There is an ongoing debate about the source and origin of the fluid flow event(s) that relate dolomitization, brecciation and primary mineralization. The debate on the origin of the fine and coarse grained dolostones includes syngenetic, diagenetic and epigenetic dolomitization theories (Misra et al., 1989). The rubble and crackle breccias that host primary mineralization are currently thought to have been formed by solution collapse during subsurface meteoric fluid flow along paleoaquifers i.e. the "paleo-aquifer hypothesis" of Harris (1971). Based on compaction and porosity features in the sedimentary rocks, Hill et al. (1971), alternatively, estimated an early Middle Ordovician age for the formation of collapse breccias. In contrast Kesler et al. (1984) suggested a single fluid source for dolomitization and mineralization in the Sweetwater, Mascot Jefferson City and Copper Ridge MVT districts in eastern Tennessee (Fig. 3.1 A) an age of between 460 and 405 Ma, from strontium isotope data.

3.3 Paleomagnetics

3.3.1 Experimental methods

The Sweetwater collection of 27 sites (382 specimens) from the EB and WB includes 8 dolostone, 11 limestone, 7 MVT mineralization and one fault breccia site (Fig. 3.1 B). It includes 108 specimens from unmineralized and mineralized clasts at 7 breccia sites (see Table 3.1). The natural remanent magnetization (NRM) was
### Table 3.1 Summary of Site Mean Remanence Data

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EB  7   149.2  29.5  4.8  156.7  
WB  12  153.8  41.8  3.4  163.6  
WB  20 % 12  151.7  37.4  3.5  156.3  
EB+WB (W-20%) 19  150.7  34.5  3.1  117.2  
O_R  3  342.8  -52.6  3.5  1210.7  
O_N  4  348.4  55.1  8.0  133.2  
MJC  7  154.6  31.1  8.5  52  

Samples: B - Ballard Pit; Rm - Riches in Mine; Ry - Ruby Quarry; T - Thompson Mines; L - Limestone; D - Dolostone; O - Ore; bx - breccia; V - vein; Ft - Fault; Cr - Copper Ridge Fm; Ct - Chepultepec Fm; Kg - Kingsport Fm; Mc - Mascot Fm. N, Nc - number of specimens measured for their NRM's and step demagnetized, and number of specimens used in site mean (also unit mean) ChRM calculation. Mean ChRM directions given by: Dec - declination; Inc - inclination; a_95 - 95% cone of confidence; and k - precision parameter. EB - Eastern belt; WB - Western belt; WB 20% - 20% unfolding; O_R - Ore (reversed ChRM directions); O_N - Ore (normal ChRM directions); MJC - Mascot-Jefferson City. * - site excluded from any statistical analysis.
measured for all specimens. The median NRM intensity of the dolomitized host rocks and mineralized specimens are 4.16 and $1.21 \times 10^{-4}$ Am$^{-1}$, respectively. One specimen from each site was thermally demagnetized in 10 steps to 500°C and a second specimen was alternating field (AF) demagnetized in 14 steps to 140 mT. Based on these initial results, most of the remaining specimens were thermally demagnetized in 13 steps to 530°C, isolating a characteristic remanence magnetization (ChRM) direction between 265° and 450°C and indicating that both pyrrhotite and magnetite are the likely ChRM carriers. However most of the thermally demagnetized specimens showed a large intensity drop between 265° and 350°C, indicating that pyrrhotite is the more important carrier. A few specimens showed intensity drops by 180°C indicating presence of goethite, which is the likely result of weathering. To remove this weathering component, the minority of remaining specimens were first demagnetized at 200°C before AF demagnetizing them in 11 steps to 140 mT. All of the sites gave a well-clustered ChRM specimen directions with a maximum angular deviation angle for the ChRM of < 15° (Kirschvink, 1980). The unit mean directions were calculated from the site means following Fisher (1953).

Saturation isothermal remanent magnetization (SIRM) analyses were done on 19 representative specimens by pulse magnetizing them in 14 steps to 900 mT and then AF demagnetizing them in 8 steps to 120 mT. The results show that the host rocks are characterized by pseudosingle to single-domain pyrrhotite and that almost all of the mineralized specimens show fine-grained hematite or goethite to be the likely remanence carrier. The presence of hematite or goethite in many of the
mineralized specimens suggest that they have been highly altered by weathering.

3.3.2 Field Tests

A breccia test (Graham, 1949) was performed on 7 sites involving 67 clasts. These sites have highly-clustered clast remanence directions with Fisher (1953) precision parameter values of $k > 25$ (Table 3.1). This indicates that the breccia clasts were altered and remagnetized after they were fixed in their present orientations. Similarly, a fold test (McElhinny, 1964) was run separately for limestone and dolostone sites in the EB and WB using 10% unfolding increments. In the EB host rock tilt corrections cause the precision parameter to decrease from 168 to 4 with the best grouping at 0% unfolding, indicating that they retain a post-folding remanence at > 99% confidence. Similarly, tilt correction for the WB host rocks causes the precision parameter to decrease from 163 to 47 and to cluster best at 20% unfolding. This suggests that the Alleghenian folding in the WB was $80 \pm 20\%$ completed at the time of magnetization.

3.4 Dolomitization and Fluid Flow

The mean ChRM direction for 7 host rock sites from the EB shows a south-southeast and moderately downward inclination, whereas for the 12 sites in the WB it shows a similar declination but a somewhat steeper inclination (Fig. 3.2 A). Site 15, which has a distinctly steeper inclination compared to other host rock sites in the WB, is an outlier and is excluded from further statistical analysis. The fold test suggests the presence of an ~ 20% synfolding remanence component in the WB
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host rocks that would have steepened the ChRM inclination in the terminal stages of the Alleghenian orogeny. Thus the best estimate for the ChRM direction is obtained by combining the mean ChRM directions from the EB uncorrected and the WB with a 20% tilt correction, which is at: declination (Dec) = 150.7°, inclination (Inc) = 34.5°, cone of 95% confidence (αₙ₉₅) = 3.1°, and precision parameter (k) = 117.2 (Fig. 3.2 A).

The pole position for the host carbonates of the Sweetwater district is at: latitude 29°N, longitude 127.5°E, with the semi-axes for its oval of 95% confidence of δp = 2.0° and δm = 3.6° (Fig. 3.2 B) that falls at 334 ± 8 Ma on the apparent polar wander path (APWP) for North America of Van der Voo (1993) and indicates that the host rocks were remagnetized during a single fluid flow event during Mississippian time. This chemical remagnetization resulted from Mississippian recrystallization erasing all evidence of a Lower Ordovician remanence. Symons and Stratakos (2002) have determined a 334 ± 14 (2σ) [334 ± 8 Ma (1σ)] paleomagnetic age for dolomitization in upper Knox carbonates of the Mascot-Jefferson City MVT district that is statistically indistinguishable from the Sweetwater dolomitization age. This concordance suggests that a single fluid flow event was responsible for dolomitization in both the MVT districts, which are about ~70 km apart in the Appalachian Valley and Ridge Province.

The site mean ChRM directions for the 7 ore sites yield two distinct populations. One population shows a mean ChRM direction (Oₙ: sites 4,5,14,22; Table 3.1) that is north-northwest and steeply downward. Its pole position at 80.6°N, 189°E, δp = 8.1° and δm = 11.4°, gives a Late Tertiary age with its oval of 95%
confidence lying along most of the Tertiary APWP path, including the present day
Earth's magnetic field direction - the obvious result of chemical weathering in these
residual Ba deposits. The existence of a Tertiary overprint is consistent with the
SIRM analyses that show that fine grained hematite or goethite is the main
remanence carrier. The $O_R$ population (sites 23,25,26; Table 3.1) gives a pole
position at $19.4^\circ N, 110.8^\circ E$, $\delta p = 3.3^\circ$, and $\delta m = 4.8^\circ$, that falls on the Late Silurian
portion of the path. However, a Silurian or prefolding and predolomitization age for
the mineralization is unrealistic. We note that the $O_R$ unit mean ChRM is based on
only 3 sites that utilize data from only half of the measured specimens. Further, an
100% tilt correction for a "prefolding" ChRM moves the pole to an impossible
position in the Pacific off the APWP. Also the SIRM analyses show that these ore
specimens are highly altered and contaminated by hematite and/or goethite. We
suggest, therefore, that the $O_R$ ChRM is an unresolvable mixture of Tertiary
hematite-borne components acquired by weathering during the frequent normal and
reversed chron of the Earth's magnetic field that characterize the Tertiary. Thus we
think that the age of the MVT mineralization at Sweetwater is unlikely to be directly
determined by paleomagnetism, given the paucity of outcrops now available, until
fresh subsurface samples become available. However, based on data from 25
highly-clustered site means, Symons and Stratakos (2002) obtained a
paleomagnetic age of 316±8 Ma for the Mascot-Jefferson City mineralization.
Dolomitization precedes mineralization in the paragenetic sequence for Sweetwater
district (Misra et al., 1989). Also, regional host rock dolomitization consistently
predates mineralization in all MVT districts worldwide where both have been dated
(Lewchuk and Symons, 1995), including Central Tennessee (Lewchuk and Symons, 1996) and Mascot-Jefferson City (Symons and Stratakos, 2002) districts of Tennessee. This argues for a younger mineralization age than $334 \pm 8$ Ma in the Sweetwater district. Given the coeval ages for dolomitization in the Sweetwater and Mascot Jefferson City MVT districts, it is probable that Sweetwater mineralization is coeval with that of Mascot-Jefferson City also.

Bachtadse et al. (1987) obtained an uncorrected coeval pole position with large error limits from 3 sites (9 samples only) from 3 mine pits in the EB, however, based on a non-significant fold test using data from well outside the Sweetwater district, they were induced to apply a 60% tilt correction and thus interpreted a Pennsylvanian age in error. The $334 \pm 8$ Ma age for dolomitization falls within the range of 408 to 320 Ma obtained by Kesler et al. (1988) using Sr isotope ratios to model fluid flow out of the Sevier shale basin and is consistent with the $347 \pm 20$ Ma Rb-Sr sphalerite age obtained by Nakai et al. (1993) for Mascot Jefferson City mineralization.

The $334\pm8$ Ma age for dolomitization in the Sweetwater district postdates the Devonian Acadian orogeny that spans from $\sim 415$ to $\sim 360$ Ma (eg. Osberg et al., 1989; Garven et al., 1993; Hamilton-Smith, 1993). With the Sweetwater and Mascot-Jefferson City districts giving a similar age for dolomitization, and also with the observed worldwide relationship between an MVT ore genesis and orogenic events in the surrounding or adjacent orogen (Symons et al., 1996; Leach et al., 2001), the age suggests that the onset of the Alleghenian Orogeny in the southern Appalachians started earlier than $334 \pm 8$ Ma and that
orogenic activity migrated northwards with time into the central and northern Appalachians, a theory suggested by Miller and Kent (1988) and later supported by Symons and Stratakos (2002). Further the 334 ± 8 Ma regional chemical remagnetization event observed in the eastern Tennessee MVT districts supports either a topographically-induced or thrust-fault driven fluid flow for ore genesis that occurred in response to Alleghenian orogenesis.

3.5 Acknowledgements

The authors thank Dr. Mike Harris of the University of Windsor and Dr. Peter J. Lemiszki, Chief Geologist, of the Tennessee Department of Environment and Conservation for assisting in sample collection, and the Natural Sciences and Engineering Research Council of Canada for grant funding to support this research.

3.6 References


CHAPTER 4

SUMMARY

4.1 Fluid Flow from Paleomagnetic Age Dates

The paleomagnetic analyses of the 359 ore and host rock specimens from the classic UMV lead-zinc MVT district indicate that dolomitization and mineralization events were about coeval at 282 ± 10 Ma. In contrast, the paleomagnetic results from 382 specimens from the enigmatic Sweetwater Ba-F-Zn Appalachian-type MVT district indicate that dolomitization, a precursor event to mineralization, occurred at 334 ± 8 Ma. These contrasting results exhibit the diversity found between the two MVT districts that is the expected consequence of varying fluid chemistry and fluid-flow paths from an orogen (Leach et al., 2001). Both of these paleomagnetic dates record a chemical remagnetization or resetting of the paleomagnetic signature from widespread regional fluid flow events during the Carboniferous and Early Permian, as McCabe and Elmore (1989) first noted. The Early Permian remagnetization in the UMV district adds substantially to the observed extent of chemical remagnetizations from fluid flow related to the Ouachitan/Alleghenian orogenies (Fig. 4.1, modified from Muttoni et al., 2001) because it is the furthest found to date from the Ouachitan/Appalachian orogen, and requires a continental-scale fluid flow for about 1000 km through the basement or undeformed platform strata of the midcontinent.

The Early Permian age for UMV dolomitization and mineralization, and the Early Carboniferous age for dolomitization in the Sweetwater district from
Fig. 4.1 Map of the North America showing location of sites remagnetized in the Cretaceous (open squares) and Carboniferous - Early Permian (solid circle). Also, shown here is the Early Permian remagnetization in the Upper Mississippi Valley (UMV) lead - zinc district (open circle with crossed lines) and Early Carboniferous remagnetization in the Sweetwater district (solid triangle). Shaded areas are fold-thrust belts (modified from Muttoni et al., 2001).
paleomagnetism correspond to tectonic events in the Ouachitan/Alleghanian orogeny. This observation strengthens the hypothesized relationship between the formation of MVT ore deposits and orogenic events in the surrounding or adjacent orogen (Symons et al., 1996; Leach et al., 2001). Further, both paleomagnetic dates for the MVT districts fit into the Devonian - Permian time window during which the majority of major MVT deposits were formed (Fig. 4.2, modified from Leach et al., 2001). This time window corresponds to the assembly of the supercontinent of Pangea, a period of intense global tectonic activity or mountain building that would be most likely to result in groundwater movement at global scales (Leach et al., 2001, and references therein).

The Early Permian age for UMV MVT mineralization and dolomitization likely corresponds to peak deformation of the Ouachitan/Alleghanian orogeny on its western side. For gravity driven fluid flow to drive fluids about a thousand kilometres through the deep sandstone aquifers of the Illinois basin into the UMV district a substantial topographic head of about 5 Km would be required and this would be best developed when the Ouachita/Appalachian orogeny uplifted the mountains to maximum elevation. The age of UMV ore genesis further complements the time-pattern model of Symons and Sangster (1994) for the MVT districts of midcontinental U.S.A. The model speculates that it takes several million years to form MVT deposits in a given district that paleomagnetic dating methods imply, and that the difference in ages of MVT districts of comparable distance from the front can be accounted for by tying fluid flow events to differing flow paths and differing periods of rapid uplift in various areas of the Ouachitan/Appalachian orogen.
### Age of MVT Deposits

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- **Host Rocks**: Represents the geological age of the host rocks for MVT deposits.
- **Paleomagnetic**: Indicates the paleomagnetic ages of the deposits.
- **Radiometric**: Denotes the radiometric ages of the deposits.

- **Paleomagnetic, this Study**: Indicates the paleomagnetic ages determined in this study.
- **Dolomitization, this study**: Denotes the dolomitization ages determined in this study.

Fig. 4.2 Distribution of radiometric and paleomagnetic ages of MVT deposits and their host rocks in the Phanerozoic. Paleomagnetic ages of dolomitization for Mascot-Jefferson City and Sweetwater districts of eastern Tennessee are shown here. The grey shaded areas represent two distinct periods of geological time when most of the major MVT deposits were formed worldwide (modified from Leach et al., 2001).
On the other hand, the Early Carboniferous paleomagnetic age of dolomitization in the Sweetwater Ba-F-Zn district corresponds to the early stages, as traditionally defined, of Alleghanian orogeny. The Sweetwater district lies in the thrust belts of the Appalachian orogen. Thus the chemical remagnetization event observed in the district could have been produced by either a topographically-induced gravity fluid flow mechanism (Garven, 1984a; Garven, 1984b) or a thrust-fault compression fluid flow mechanism (Oliver, 1986) that occurred in response to Alleghanian orogenesis.

4.2 The Paleomagnetic Method: Conclusion

The paleomagnetic results for the timing of dolomitization and mineralization in the UMV district and of dolomitization in the Sweetwater district are well constrained and consistent with age dates from other studies. The dates for the two MVT districts of this study add to the database for MVT deposits worldwide that have been dated by radiometric and paleomagnetic methods (Fig. 4.2, modified from Leach et al., 2001) The paleomagnetic method continues to prove to be an efficient tool for defining the age of fluid flow events that cause dolomitization and MVT ore mineralization in carbonate host rocks.

4.3 References


APPENDIX A: ADDITIONAL FIGURES FOR SWEETWATER DISTRICT

Attached in the next five pages are the additional figures for the Sweetwater district collection. The submitted version that appears in Chapter 3 consists only two figures and one table because of the four journal page restriction of the manuscript.

A1 Orthogonal AF step demagnetization plots for example specimens of limestone and dolostone.

A2 Orthogonal thermal step demagnetization plots for example specimens of limestone and dolostone.

A3 Orthogonal AF and thermal step demagnetization plots for example specimens of mineralization.

A4 SIRM acquisition and demagnetization plots for limestone and dolostone specimens.

A5 SIRM acquisition and demagnetization plots for mineralized specimens.
A1 Orthogonal AF step demagnetization plots for example specimens of limestone from (a) site 01 in EB and (b) site 10 in WB, and dolostone from (c) site 02 in EB and from (d) site 11 in WB, with a Kiaman reversed polarity remanence. A 200°C thermal step is done on few specimens to remove the goethite weathering component. The axes are north (N), east (E), south (S), west (W), up (U) and down (D) with points in the horizontal and vertical planes denoted by circles and triangles, respectively. The axial values are proportionate to the NRM intensity. The labelled steps are in milliTesla (mT). EB - Eastern Belt, WB - Western Belt.
A2 Orthogonal thermal step demagnetization plots for examples specimens of limestone from (a) site 01 in EB and (b) site 16 in WB, and dolostone from (c) site 03 in EB and from (d) site 21 in WB, with a Kiaman reversed polarity remanence. Conventions as in appendix A.1, except the labelled steps are in degree celsius (°C).
A3 Orthogonal AF (a,b) and thermal (c,d) step demagnetization plots for examples specimens of mineralized specimens from (a) site 22, (b) site 14, (c) site 05, (d) site 26, with reversed polarity (b,d) and normal (a,c) polarity remanence directions. The mineralized specimens show a unresolved residual component that prevents decay to the origin of the plot. The labelled steps for a,b (c,d) are in milliTesla (Degree Celsius, °C). Other conventions as in appendix A.1.
A4 SIRM acquisition and demagnetization cross-over plots for (a) limestone and (b) dolostone specimens shown as solid lines. $J/J_{900}$ is the ratio of the measured to SIRM intensity at 900 mT. H is the magnetic field intensity in milliTesla (mT). Dashed and dotted lines represent the type curves for single (SD), pseudosingle (PSD) and multidomain (MD) pyrrhotite and magnetite respectively.
A5 SIRM acquisition and demagnetization cross-over plots for mineralized specimens shown as solid lines plotted on two different sets of type curves. (a) Dotted (dashed) lines represent the type curves for single (SD) and pseudosingle (PSD) goethite (hematite) respectively. (b) Dotted (dashed) lines represent SD and PSD pyrrhotite (hematite) respectively. Conventions as in appendix A.4.
APPENDIX B: DECLARATIONS OF CO-AUTHORSHIP CONTRIBUTIONS

Attached in the next three pages are co-author declarations from D.T.A. Symons, D.F. Sangster, and Kula C. Misra concerning their involvement with the submitted versions of Chapters 2 and 3.
DECLARATION OF CO-AUTHOR CONTRIBUTION

I acknowledge and give personal consent to the use of information in the following manuscripts, which have been submitted for publication, to be included in the M.Sc thesis of Shanmugam Johari Pannalal:


My intellectual contribution to the work reported in these manuscripts was the formulation of basic research plan to study the Mississippi Valley-type ore deposits from the Upper Mississippi Valley and Sweetwater Ba-F-Zn districts of U.S.A using paleomagnetism to determine the timing of dolomitization and mineralization and to assist in sample collecting. I contributed guidance to the writing of the manuscripts only. As Mr. Pannalal's thesis supervisor, my financial contribution to the funding of the work carried out in Upper Mississippi Valley, Sweetwater and at the University of Windsor was 100% from my Natural Sciences and Engineering Research Council of Canada and Research grants.

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Date: Aug 14/02

Witness: [Signature]

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My intellectual contribution to the work reported in this manuscript was guidance on writing the introduction and the discussion sections of the paper. I also assisted in the planning and collecting of samples.

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My intellectual contribution to the work reported in this manuscript was guidance on writing and reviewing the paper. I also assisted in the planning and collection of samples.

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Date: July 29, 2002

Witness: [Signature]
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Zn district, eastern Tennessee: a paleomagnetic age for dolomitisation from fluid