Electron microscopic and rock magnetic study of remagnetized Leadville carbonates, central Colorado

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Abstract

Thermal demagnetization of limestone and dolomite samples from the Lower Carboniferous Leadville Formation of central Colorado reveals four magnetization components, of which three (A, B, and C) are ancient. The syn-folding A component is found both in limestone and dolomite below about 350°C and yields a paleopole at 71.6°N, 203.3°E, near the Late Cretaceous to early Tertiary segment of the North American APWP. The B component is found only in the limestone and has a pole position at 68.5°N, 138.1°E in situ, and 51.6°N, 136.9°E after tilt correction. The in-situ pole and partially tilt-corrected poles (up to about 30% unfolding) resemble Middle–Late Jurassic paleopoles of cratonic North America. The C component is found only in the dolomite with paleopoles at 45.7°N, 110.0°E (in situ) and at 50.7°N, 112.8°E (after tilt correction). These poles fall near the Permian segment of the apparent polar wander path. The corresponding ages of these three magnetizations therefore are all younger than Early Carboniferous, indicating that they are all secondary magnetizations. A rock magnetic and electron microscope study was successful in linking these multiple remagnetizations to identifiable magnetic mineral carriers, which helps to infer the authigenesis in the carbonates. Unblocking temperatures of the natural remanent magnetizations (NRM) and three-component isothermal remanent magnetizations (3D-IRM) indicate that pyrrhotite and magnetite are the major magnetic carriers of the NRM. Electron microscopy of magnetic extracts revealed magnetite spherules and fine-grained magnetite growing on quartz, albite, and chlorite, whereas electron microscopy of thin sections revealed goethite, hematite, pyrite and pyrrhotite in addition to magnetite. Demagnetization characteristics of NRM and rock magnetic experiments are inconsistent with hematite or goethite carrying a detectable ancient remanent magnetization, and the magnetite spherules are unlikely to carry any magnetization other than the recent magnetic overprint. Pyrrhotite is a likely chemical remanence carrier of the Late Cretaceous–early Tertiary A magnetization in both dolomite and limestone samples. Non-spheroidal iron oxides are observed in scanning and transmission electron microscopy in three forms: (1) as grains on the boundary of residual dolomite and dedolomite, inferred to be magnetite and carrying the B magnetization; formation of this magnetite appears to be related to Jurassic dedolomitization; (2) as fine-grained iron oxide inclusions within calcite, dolomite, or bitumen veins; or (3) as fine-grained magnetite growing on secondary minerals such as quartz, albite, and chlorite. The inclusions in dolomite have been shown by selected-area electron diffraction (SAED) to be magnetite and are inferred to carry the C magnetization acquired during late Paleozoic dolomitization; the iron oxide inclusions in calcite and bitumen resemble those in the dolomite and may also be magnetite, but they could not be analyzed by SAED. The fine-grained magnetite growing on secondary minerals, surprisingly, contains small amounts of titanium and manganese; this observation has to our knowledge not been reported before for authigenic...
magnetite. The ulvöspinel content (x) in these titanomagnetites (Fe$_{1-x}$Ti$_x$O$_4$) ranges from 0 to 0.15. This study shows that electron microscope observations can successfully identify some of the magnetic carriers in multiply remagnetized carbonates, even if they are submicrometer in size. © 1998 Elsevier Science B.V. All rights reserved.

**Keywords:** remagnetization; Laramide orogeny; pyrrhotite; authigenesis; (titano-)magnetite

1. Introduction

With the advent of sensitive cryogenic magnetometers, carbonate rocks have increasingly been investigated in paleomagnetic studies aimed at elucidating magnetostratigraphy, tectonic reconstructions, or even geomagnetic field behavior. However, it is now widely recognized that many cratonic carbonate rocks carry only secondary (albeit ancient) magnetizations (e.g., McCabe et al., 1983, 1988; Horton et al., 1984; Elmore et al., 1985; McCabe and Elmore, 1989; Elmore and McCabe, 1991; Jackson et al., 1992). Interpretations of carbonate paleomagnetic records, therefore, depend critically on knowledge about the timing and mechanism of acquisition of the natural remanent magnetization (NRM), including post-depositional modifications. Much of the work in the last decade has been directed at determination of the mechanism of remagnetization of these carbonate rocks and the relationship between remagnetization and geologic events, with the result that many causes of remagnetization have been proposed. They include: interaction between the rocks and migrating basinal or orogenic fluids (e.g., McCabe et al., 1989), interactions with mineralizing fluids (e.g., Symons and Sangster, 1992), or with hydrocarbons (e.g., Elmore and Crawford, 1990), thermal resetting or thermochemical remagnetization related to nearby intrusions (e.g., Horton et al., 1984), as well as oxidation of siderite (e.g., Ellwood et al., 1988), dolomitization (e.g., Hart and Fuller, 1988), and dedolomitization (Loucks and Elmore, 1986). However, several of these factors may be interdependent and not a single one has been established unambiguously as a dominant cause because of a lack of direct evidence (McCabe et al., 1989). In order to make progress in establishing the processes that have led to the widespread remagnetization of ancient carbonate rocks, identification by electron microscopy of potentially magnetic minerals forms an important link between paleomagnetic and rock magnetic studies.

Horton et al. (1984) reported paleomagnetic data for Lower Carboniferous dolomites of the Leadville Formation in central Colorado and interpreted the magnetizations as being of two different ages corresponding to two events: (1) late Paleozoic dolomitization, and (2) Tertiary thermochemical activity related to intrusions. The limestones of the Leadville Formation also were interpreted as being remagnetized in the Tertiary, even though they were not close to intrusive centers. Thus, it occurred to us that the Leadville Formation offered an interesting opportunity to study the relations between diagenesis, regional dolomitization, Tertiary igneous activity, Laramide deformation, and remagnetizations, because previous studies involving electron microscopy of remagnetized carbonates (Lu et al., 1990; Suk et al., 1991, 1993a,b) had generally been restricted to rocks that have been remagnetized only once. We were especially motivated by the hypothesis of Horton and colleagues that the multiple remagnetizations occurred because of two different processes, one thermal (or thermochemical), the other chemical and related to dolomitization.

The Pennsylvanian Belden Formation, which overlies the Leadville Formation, has been studied by Fruit et al. (1995) and Banerjee et al. (1997). They inferred that the Belden Formation is remagnetized with variable ages ranging from late Paleozoic to early Tertiary. Their intermediate unblocking temperature component of Tertiary (syn-folding) age is interpreted as a thermoviscous remanent magnetization carried by magnetite, whereas the higher-temperature remagnetization of late Paleozoic to Cretaceous age is interpreted by Banerjee et al. (1997) as a chemical remanence also carried by magnetite, which formed during burial diagenesis. These interpretations broadly agree with those of Horton et al. (1984) for the Leadville carbonates, albeit with some refinements in that Banerjee et al. argue for a variable age of the earlier (pre-Tertiary) remagnetization, relating it to organic matter maturation and
not to dolomitization. Whereas many similarities exist between the paleomagnetic results of the Belden Formation and those of our study, as is made apparent by this paper, there are important differences in our preferred mechanisms for the Tertiary remagnetization, compared to those proposed by Horton et al. (1984) and Banerjee et al. (1997). Our differing interpretation is based on our electron-microscopic identification of a different magnetic mineral (pyrrhotite) carrying the Tertiary component.

2. Geologic background

The Lower Mississipian Leadville Formation of central Colorado is well exposed around the Sawatch uplift (Fig. 1) and is predominantly composed of platform carbonates deposited in shallow subtidal environments. During Late Mississipian time, a regionally extensive karst plain developed on Lower Mississipian shelf carbonates in the Rocky Mountain states from Montana to New Mexico (De Voto, 1980, 1987; Sando, 1987). Central Colorado was fragmented into a foreland mosaic of fault blocks while the late Paleozoic Ouachita-Marathon orogeny occurred along the southern border of the North American craton (Kluth and Coney, 1981; De Voto, 1990). Tectonic activity on the faults produced a sedimentary and structural basin in north-central Colorado that was bounded on the northeast and southwest by the ancestral Front Range and the Uncompahgre Highland, respectively. This basin is thought to have been bisected partly by the intervening Sawatch uplift (Wallace, 1990). Uplift and subsidence, initially related to the Ouachita-Marathon orogeny, persisted until the Late Triassic. Tectonism during the remainder of the Mesozoic was largely related to regional epeirogenic events induced by orogenic activity along the western margin of the continent, including the uplift of local highlands caused by movement along faults in the Jurassic. It is inferred that subduction-related magmatism and uplift again affected the region during the Late Cretaceous–early Tertiary Laramide orogeny (Wallace, 1990). From this history, it is inferred that structural deformation (folding, tilting) of the Leadville Formation occurred in multiple phases, including episodes related to the late Paleozoic Ouachita and the Late Cretaceous–early Tertiary Laramide orogenies.

Sulphide mineralization occurred in the Leadville Formation and the overlying Upper Carboniferous Belden Formation in the area between the dashed lines of Fig. 1. The timing of this carbonate-hosted mineralization is generally thought to be mid-Tertiary (Beaty et al., 1990), but Tschauder et al. (1990) have argued that some of the ores are Mississippian (pre-Belden Fm.), whereas they believed others to be Tertiary in age.

3. Site and sample description

Samples were collected from twelve sites distributed over four localities at the northeastern end of the Sawatch uplift (Fig. 1). At least five samples (2.5 cm in diameter) were drilled and oriented with a compass at closely spaced stratigraphic intervals at each site and cut into specimens of 2.2 cm length in the laboratory. Thin sections for mineralogic and petrologic study were cut directly from the cores. A
few bulk rock samples (weight about 10 kg) were collected from each locality and used for extraction of magnetic minerals.

The samples are limestones at the northern eight sites near Minturn (Fig. 1), whereas to the south, in a belt along the eastern flank of the Sawatch uplift, the Leadville Formation has been regionally altered to massive dolomite that hosts numerous Pb–Zn–Ag ore deposits, e.g., in the Leadville–Gilman area. The dolomite samples were collected at four sites on the east flank of the Sawatch uplift near Tennessee Pass (Fig. 1). These dolomites are fine- to medium-grained, and contain some chert nodules. The limestones from the Minturn area are predominantly pelletal, oolitic, or mixed skeletal, although some are dedolomites.

Hydrocarbon (or bitumen) fills pore spaces and occurs in stylolites in several samples from sites 4 and 6 of the Minturn area (Fig. 2A). Some bitumen seams are cut by later calcite veins (Fig. 2B), which are of two types, one with and the other without goethite. The brown color induced by the goethite allows easy differentiation of calcite in the two types of veins.

4. Methods

4.1. Paleomagnetism and rock magnetism

Measurements of natural remanent magnetization (NRM) were carried out with a ScT cryogenic magnetometer, with alternating field (AF) and thermal demagnetization performed with Schonstedt equipment at the University of Michigan, in a shielded room with rest field generally less than 200 nT. Demagnetization results were plotted in stereographic projections and orthogonal vector diagrams (Zijderveld, 1967). Directions of components of magnetization were determined with principal component analysis (Kirschvink, 1980). Pilot AF and thermal demagnetization techniques showed that AF effectively reduces the intensity to near-zero in fields up to 200 mT, but that thermal treatment was preferable because it provided better resolution of the demagnetization trajectories.

For magnetic characterization of Leadville carbonate samples, acquisition of saturation isothermal remanent magnetization (SIRM), acquisition and AF demagnetization of IRM and anhysteretic remanent magnetization (ARM) for a modified Lowrie–Fuller (L–F) test (Lowrie and Fuller, 1971; Johnson et al., 1975) were carried out for representative samples at the paleomagnetic laboratory of the University of Michigan to identify the magnetic mineralogy, dominant grain sizes and domain state, and magnetic interactions among magnetic minerals. The ARM was induced using a 100 mT AF peak field with a 0.1 mT direct field (DC) bias, and the IRM was acquired using a 100 mT DC field. These laboratory-induced magnetizations were demagnetized in a Schonstedt AF demagnetizer up to a peak induction field of 100 mT for the modified Lowrie–Fuller test. Saturation IRM acquisition curves were obtained by subjecting samples to increasing fields in twelve steps to a maximum of 1.4 T. A partial ARM (pARM) was also imparted on the specimens using a pARM switching device that turns on and off a DC bias field at preset points for a given window of alternating fields in a conventional AF demagnetizer (Jackson et al., 1988).

Thermal demagnetization of three-component (3D-)IRM (Lowrie, 1990) was used to correlate between unblocking temperatures and coercivities, in order to aid in identification of the ferromagnetic minerals in the carbonate samples. The IRM was first imparted in the maximum available magnetization field (1.4 T) along the z-axis of the samples. Almost all magnetic minerals were thus magnetized in the direction of the maximum field. Next, a field of 0.3 T was applied along the y-axis, so that the magnetic minerals with remanent coercivities <0.3 T, such as magnetite and pyrrhotite, were remagnetized leaving only the higher-coercivity minerals magnetized along the z-axis. Subsequently, a field of 0.12 T was applied along the x-axis, remagnetizing the softest magnetic minerals, such as larger-grained magnetite. Samples were then thermally demagnetized in a magnetic field-free space. The remanent magnetizations corresponding to the three orthogonal directions were then plotted as a function of temperature.

Hysteresis properties of bulk rock samples were measured on an alternating gradient force magnetometer (AGFM) in the Institute for Rock Magnetism at the University of Minnesota. The magnetic mo-
Fig. 2. Optical microscopic images (plain light) of Leadville limestone sample: (A) stylolite filled with bitumen; (B) some bitumen seams cut by a calcite vein.
ments of samples given a low-temperature IRM were measured with a Quantum Design MPMS2 cryogenic magnetometer also at the Institute for Rock Magnetism at the University of Minnesota.

4.2. Electron microscopy

Magnetic extracts from large limestone samples were prepared by dissolution of crushed bulk rock in dilute buffered acetic acid (McCabe et al., 1983), followed by separation of the magnetic component from the insoluble residue with a rare-earth permanent magnet.

‘Sticky-wax’-mounted thin sections were also made for each sample and used for preliminary petrographic studies by optical microscopy and scanning electron microscopy (SEM). SEM data were obtained with a Hitachi S-570 SEM fitted with a back-scattered electron (BSE) detector and a Kevex Quantum detector for analysis of energy-dispersive spectra (EDS) of elements of atomic number > 5.

Samples used for scanning transmission electron microscope (STEM) and analytical electron microscopy (AEM) analyses were prepared by ion-mill thinning of selected areas of thin sections. A Philips CM12 STEM equipped with a Kevex Quantum detector and operated at 120 kV was used for the STEM/AEM analyses. Selected-area electron diffraction (SAED) patterns and bright-field images were obtained in transmission electron microscope (TEM) mode. AEM analyses were obtained in scanning mode, which gave rise to an electron beam approximately 50 Å in diameter, by rastering the beam over areas of 200 by 1000 Å at thin edges of the specimens. Grains as small as 200 Å across could therefore be analyzed without beam overlap on other phases. Specimens were tilted toward the detector by 20° giving an X-ray take-off angle of 34°. The X-ray spectra were acquired at a rate of 100–300 cps for 200 s (live time).

5. Results

5.1. NRM characteristics

The samples have NRM intensities ranging from 0.1 to 5.6 mA/m, with the limestones typically revealing higher intensities than the dolomite samples. Each of the sites exhibits fairly uniform demagnetization behavior. Thus, thermal demagnetization was performed on only five samples from each site, which was sufficient to characterize the directions of magnetization. Thermal demagnetization of NRM of limestone samples collected from two localities (eight sites) near Minturn shows that they possess two ancient magnetizations (A’ and B), which are commonly overprinted by a nearly antipodal component with unblocking temperatures <200°C and coercivities <10 mT (Fig. 3A,B). This overprint conforms to the present-day field (pdf) direction in Colorado and is interpreted as a recent viscous magnetization. Component A’ has a southerly declination and steep negative inclination in thermal demagnetization between 200° and 400°C (Fig. 3A; Table 1). This A’ component has an inclination that clearly is steeper than that of the magnetization isolated above 400°C. In contrast, AF demagnetization treatment of limestone samples shows a barely noticeable difference in inclination between a lower-coercivity (<55 mT) component and a higher-coercivity component (from 70 to 200 mT, see Fig. 3B), which has a slightly steeper inclination. The latter result is identical to AF results published earlier (Horton and Geissman, 1990, fig. 5D). The higher-coercivity component with the steeper inclination appears to represent the A’ component removed during thermal demagnetization, whereas the lower-coercivity component with its slightly lower inclination is interpreted as the simultaneous removal of the A’ and B components.

Principal component analysis of component A’ from a total of 40 samples yielded a mean...
Paleomagnetic results of component A′ from Leadville limestone (site location: 39.8°N, 106.4°W)

<table>
<thead>
<tr>
<th>Site</th>
<th>Strike/dip</th>
<th>n/N</th>
<th>Declination/inclination (°) in situ</th>
<th>k</th>
<th>α95 (°)</th>
<th>Pole position</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn-1</td>
<td>210/23</td>
<td>5/5</td>
<td>195.7/−69.2</td>
<td>157.6/−55.7</td>
<td>202.1</td>
<td>5.4</td>
</tr>
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<td>Mn-2</td>
<td>210/23</td>
<td>5/5</td>
<td>189.2/−74.5</td>
<td>148.3/−58.2</td>
<td>119.1</td>
<td>7.0</td>
</tr>
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<td>Mn-3</td>
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<td>5/5</td>
<td>187.7/−78.5</td>
<td>141.3/−60.7</td>
<td>65.0</td>
<td>9.6</td>
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<td>Mn-4</td>
<td>200/23</td>
<td>5/5</td>
<td>195.0/−70.1</td>
<td>150.7/−58.6</td>
<td>48.8</td>
<td>11.1</td>
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<td>Mn-5</td>
<td>190/24</td>
<td>5/5</td>
<td>165.9/−68.7</td>
<td>132.8/−52.3</td>
<td>29.8</td>
<td>14.2</td>
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<td>Mn-6</td>
<td>175/24</td>
<td>5/5</td>
<td>196.9/−52.0</td>
<td>164.0/−54.4</td>
<td>89.9</td>
<td>8.1</td>
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<td>Mn-7</td>
<td>175/24</td>
<td>5/5</td>
<td>173.8/−66.4</td>
<td>131.4/−56.5</td>
<td>114.5</td>
<td>7.2</td>
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<tr>
<td>Mn-8</td>
<td>175/24</td>
<td>5/5</td>
<td>171.1/−63.9</td>
<td>133.2/−53.9</td>
<td>133.4</td>
<td>6.6</td>
</tr>
<tr>
<td>Mean (in situ)</td>
<td>8/8</td>
<td>&amp; 184.6/−68.4</td>
<td>77.5</td>
<td>6.3</td>
<td>77.8°N, 267.2°E</td>
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<tr>
<td>Mean (tilt corrected)</td>
<td>8/8</td>
<td>144.8/−56.8</td>
<td>119.4</td>
<td>5.1</td>
<td>62.6°N, 169.9°E</td>
<td></td>
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</tbody>
</table>

Strike follows the left-hand rule, such that it is the dip direction minus 90°. n = number of samples used in the statistical analysis, and N = numbers demagnetized.

decidation/inclination \((D/I) = 184.6°/−68.4°, k = 77.5, \alpha_{95} = 6.3° (in situ), and 144.8°/−56.8°, k = 119.4, \alpha_{95} = 5.1° (after simple tilt correction). Principal component analysis of component B from a total of 34 samples yielded an in-situ \(D/I = 157.9°/−47.1°, k = 212.8, \alpha_{95} = 4.1°, and an after tilt correction \(D/I = 144.6°/−31.0°, k = 267.5, \alpha_{95} = 3.7° (Table 2). The poles calculated for these components are also given in Tables 1 and 2.

Dolomite samples from the Tennessee Pass area also possess three magnetization components: one is labeled component A″ and is similar to component A′ of the Leadville limestone at Minturn; the second, herein called component C, has south-southeast declinations and shallow negative inclinations (Fig. 3C); the third is the low-temperature, low-coercivity (pdf) overprint seen in all samples, consistent with data of Horton et al. (1984). Both the A″ and C components show dual polarities (Fig. 3C,D). Principal component analysis of component A′ from a total of 20 samples yields \(D/I = 155.4°/−64.7° (in situ, k = 34.8, \alpha_{95} = 15.8° and 173.6°/−74.4, k = 16.0, \alpha_{95} = 23.7° (after tilt correction). Principal component analysis of C directions from a total of 19 samples yields \(D/I = 155.6°/−2.0°, k = 54, \alpha_{95} = 12.6° (in situ), and 156.3°/−12.5°, k = 54, \alpha_{95} = 12.7° (after tilt correction). Mean directions and corresponding paleopoles are listed in Tables 3 and 4.

Unblocking temperatures of components A′ and A″ are <350°C, which may imply iron sulfide as
Table 3
Paleomagnetic results of component A" from Leadville dolomite (site location: 39.3°N, 106.3°W)

<table>
<thead>
<tr>
<th>Site</th>
<th>Strike/dip</th>
<th>n/N</th>
<th>Declination/inclination (°)</th>
<th>k</th>
<th>a95 (°)</th>
<th>Pole position</th>
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<tbody>
<tr>
<td></td>
<td></td>
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<td>in situ tilt corrected</td>
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<tr>
<td>Ld-1</td>
<td>25/18</td>
<td>5/5</td>
<td>172.1/-61.8</td>
<td>209.1/-66.6</td>
<td>148.6</td>
<td>6.3</td>
</tr>
<tr>
<td>Ld-2</td>
<td>25/18</td>
<td>5/5</td>
<td>184.2/-58.1</td>
<td>214.6/-59.9</td>
<td>717.7</td>
<td>2.9</td>
</tr>
<tr>
<td>Ld-3</td>
<td>80/7.5</td>
<td>5/5</td>
<td>303.3/+63.6</td>
<td>289.8/+68.1</td>
<td>313.2</td>
<td>4.3</td>
</tr>
<tr>
<td>Ld-4</td>
<td>70/10</td>
<td>5/5</td>
<td>313.6/+65.7</td>
<td>298.2/+74.1</td>
<td>241.0</td>
<td>4.9</td>
</tr>
<tr>
<td>Mean</td>
<td>(in situ)</td>
<td>4/4</td>
<td>155.4/-64.7</td>
<td>34.8</td>
<td>15.8</td>
<td>70.7°N, 193.9°E</td>
</tr>
<tr>
<td>Mean</td>
<td>(tilt corrected)</td>
<td>4/4</td>
<td>173.6/-74.4</td>
<td>16.0</td>
<td>23.7</td>
<td>68.1°N, 245.3°E</td>
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Strike follows the left-hand rule, such that it is the dip direction minus 90°. n = number of samples used in the statistical analysis, and N = numbers demagnetized.

the principal carrier of this component. The maximum unblocking temperatures of components B and C (e.g., Fig. 3) are all <580°C, whereas typical coercivities in AF demagnetization are <70 mT, implying magnetite as the principal carrier of these two components. AF and thermal demagnetization characteristics are inconsistent with goethite or hematite as significant magnetization carriers for the A', A", B, and C magnetizations.

Because the limestone and dolomite localities are each from a monocline, and because component B is only found in samples at one monocline whereas component C is only found at the other, fold tests cannot be carried out for components B and C. A fold test on the combined A' and A" magnetizations from limestone and dolomite samples revealed that the best grouping of directions is obtained after 30% bedding tilt (maximum k in Fig. 3E). The calculated f value (not shown) of the tilt test by McFadden and Jones (1981) is 0.111 and less than the critical value of 0.3493, the F distribution (with 7 and 3 degrees of freedom) at the 95% level of confidence. The fold tests therefore indicate that the A' and A" magnetizations may well be of the same age and could have been acquired between different folding phases. The 30% tilt correction yields a mean for the combined A magnetization of D/I = 165.9°/167.0° (k = 58.1, a95 = 5.7°) and a paleopole at 71.6°N, 203.3°E.

5.2. Electron microscopic observations of iron-bearing minerals

This section is divided into three parts, dealing successively with observations made on iron oxides obtained from magnetic extracts, observations made on thin sections containing sulfides and oxides other than magnetite, and observations made on thin sections containing magnetite. The observations are summarized in Table 5, for easy reference.

Table 4
Paleomagnetic results of component C from Leadville dolomite (site location: 39.3°N, 106.3°W)

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<th>Site</th>
<th>Strike/dip</th>
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<td>in situ tilt corrected</td>
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<td></td>
</tr>
<tr>
<td>Ld-1</td>
<td>25/18</td>
<td>4/5</td>
<td>159.8/-3.9</td>
<td>162.2/-16.5</td>
<td>63.6</td>
<td>8.5</td>
</tr>
<tr>
<td>Ld-2</td>
<td>25/18</td>
<td>5/5</td>
<td>161.7/+1.1</td>
<td>162.9/-11.2</td>
<td>58.7</td>
<td>7.7</td>
</tr>
<tr>
<td>Ld-3</td>
<td>80/7.5</td>
<td>5/5</td>
<td>144.2/-11.7</td>
<td>143.3/-18.4</td>
<td>25.3</td>
<td>5.3</td>
</tr>
<tr>
<td>Ld-4</td>
<td>70/10</td>
<td>5/5</td>
<td>156.5/+6.7</td>
<td>156.4/-3.3</td>
<td>27.9</td>
<td>14.7</td>
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<tr>
<td>Mean</td>
<td>(in situ)</td>
<td>4/4</td>
<td>155.6/-2.0</td>
<td>54</td>
<td>12.6</td>
<td>45.7°N, 110.0°E</td>
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<tr>
<td>Mean</td>
<td>(tilt corrected)</td>
<td>4/4</td>
<td>156.3/-12.5</td>
<td>54</td>
<td>12.7</td>
<td>50.7°N, 112.8°E</td>
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</table>

Strike follows the left-hand rule, such that it is the dip direction minus 90°. n = number of samples used in the statistical analysis, and N = numbers demagnetized.
Table 5
Possibly magnetic minerals observed in the carbonates of the Leadville Formation

<table>
<thead>
<tr>
<th>Magnetic extracts</th>
<th>Limestone (A’ and B components)</th>
<th>Dolomite (A” and C components)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>studied by</td>
<td>mineral comp.?</td>
</tr>
<tr>
<td></td>
<td>SEM</td>
<td>STEM</td>
</tr>
<tr>
<td>Spherules</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Fine-grained Ti–Fe-oxides</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Thin sections</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron oxides next to sulfide</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Iron oxide next to dolomite–dedolomite boundaries</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>Iron oxide in bitumen seams</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>Subhedral iron oxides</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Iron oxide inclusions</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>Iron sulfide inclusions</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>Goethite in pore spaces</td>
<td>yes</td>
<td>no</td>
</tr>
</tbody>
</table>

‘–’ = not observed or not a carrier of the NRM; ‘?’ = uncertain determination or uncertain remanence carrier; ‘no’ means that the mineral phase was not characterized by STEM. Gtt = goethite; Po = pyrrhotite; Py = pyrite; Mte = magnetite; Hem = hematite; pdf = present-day field direction (viscous remanence).

5.2.1. SEM/STEM observation of magnetic extracts

Magnetite spherules with grain sizes ranging from 5 to 85 μm in limestone samples of the Leadville Formation have been described previously (Xu et al., 1994). They were extracted as magnetic separates from the insoluble residue. Magnetite spherules extracted from dolomite samples of the Leadville Formation were also reported by Horton et al. (1984). Our SEM observations of these spherules showed that there are two kinds of surface textures (smooth and patterned). SAED patterns from fragments and platelets of both kinds of spherules indicated that they are composed of single-crystal magnetite grains. The vast majority of these magnetite spherules, however, were patterned and were deemed incapable of carrying ancient remanent magnetizations based on a comparison of the coercivities of the NRM in samples of the Leadville Formation and those of the magnetite spherules (Xu et al., 1994). For spherules extracted from Appalachian remagnetized carbonates, however, this conclusion is less firm (Suk and Halgedahl, 1996).

A second commonly observed magnetic component of the insoluble residue of the limestones consists of fine-grained iron oxide grains that have grown on quartz, albite, and chlorite (Fig. 4A,B). These iron oxides have grain sizes ranging from 0.1 to 5 μm. Because SEM magnification of images of such fine-grained minerals is limited, magnetic separates were crushed and then mounted on holey-carbon coated copper grids for STEM observation. A TEM bright-field image of crushed magnetic extracts reveals euhedral magnetite grains, <1 μm in diameter (for example, grown on albite; Fig. 4C). Thin edges of these fine-grained oxides give SAED patterns with sharp diffraction spots (Fig. 4D) that are characteristic of single-crystal magnetite.

EDS from some fine-grained magnetite grains contain clear indications of Ti and minor Mn in addition to Fe. X-ray mapping shows that the distribution of Ti in the grains is nearly homogeneous, indicating that these fine-grained magnetites are solid solutions of magnetite and ulvöspinel ($(1 – x)Fe_3O_4 – xFe_2O_4$). The x-value varies between 0 and 0.15.

Fig. 4. Electron microscope images of fine-grained magnetite from magnetic extracts. (A) BSE photograph showing fine-grained magnetite on albite. (B) BSE photograph showing fine-grained magnetite (arrows) on quartz. (C) STEM bright-field image of a euhedral low-Ti-magnetite grain growing on an albite grain. (D) SAED pattern showing that the dark grain of (C) is a single-crystal magnetite. Mt = magnetite; Ab = albite.
Table 6
Selected typical analytical electron microscopy (AEM) analyses of fine-grained magnetite growing on albite, quartz, and chlorite (cation numbers calculated on the basis of 4 O).

<table>
<thead>
<tr>
<th></th>
<th>mt 1</th>
<th>mt 2</th>
<th>mt 3</th>
<th>mt 4</th>
<th>mt 5</th>
<th>mt 6</th>
<th>mt 7</th>
<th>mt 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>0.077</td>
<td>0.089</td>
<td>0.135</td>
<td>0.026</td>
<td>0.049</td>
<td>0.068</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Mn</td>
<td>0.039</td>
<td>0.013</td>
<td>0.055</td>
<td>0.068</td>
<td>0.017</td>
<td>0.047</td>
<td>0.047</td>
<td>0.046</td>
</tr>
<tr>
<td>Fe</td>
<td>2.538</td>
<td>2.539</td>
<td>2.450</td>
<td>2.512</td>
<td>2.590</td>
<td>2.293</td>
<td>2.635</td>
<td>2.636</td>
</tr>
<tr>
<td>Total</td>
<td>2.654</td>
<td>2.641</td>
<td>2.640</td>
<td>2.662</td>
<td>2.656</td>
<td>2.521</td>
<td>2.682</td>
<td>2.682</td>
</tr>
</tbody>
</table>

mt 1–8 represent eight different grains analyzed; Fe represented as total iron (Fe$^{2+}$ and Fe$^{3+}$).

for different grains (Table 6), but it is constant for different areas of the same grain, within error.

5.2.2. SEM/STEM observation of thin sections
Minerals other than magnetite. Pyrite, pyrrhotite, goethite and hematite have all been observed with SEM/STEM techniques in thin sections. They occur in the following modes.

(1) Iron oxide (goethite) next to iron sulfides (pyrite and pyrrhotite) in limestones. Many irregular iron oxide grains with iron sulfide interiors have been observed in limestone samples from the Minturn locality (Fig. 5A); these combinations have also been reported for the overlying Belden Formation (Banerjee et al., 1997). They can also occur in yellow-brown colored, late calcite veins that cross-cut bitumen seams in the limestones (Fig. 2B). Some grains show well developed crystal shapes (Fig. 5A). EDS analyses show no cations other than iron. It is not possible to distinguish among magnetite, hematite, and goethite by SEM because conventional EDS analyses do not produce accurate Fe/O ratios. However, because TEM can give diffraction patterns that characterize crystal structure, a few irregular iron oxide grains with iron sulfide cores were crushed and mounted on holey-carbon coated copper grids for TEM observation. AEM analyses confirmed that these grains are composed of iron oxide and iron sulfides. Iron oxide grains gave SAED patterns consistent only with polycrystalline goethite (Fig. 5B,C). Two types of iron sulfides were detected (Fig. 5D), one having a sulfur peak twice that of iron (Fig. 5E) consistent with typical EDS of pyrite, whereas the EDS from the grey areas have a sulfur peak smaller than that of iron (Fig. 5F), consistent with the composition of pyrrhotite.

(2) Euhedral or subhedral iron oxides (hematite and goethite) in dolomite. Euhedral or subhedral iron oxides with grain sizes of 10 to 80 μm have been observed in a few thin sections of dolomite from the Leadville Formation (Fig. 6A,B). These iron oxide grains can generally be observed with an optical microscope as occurring between dolomite crystals. BSE images show two levels of contrast indicating the presence of two different iron oxides within a single grain (Fig. 6C). Hematite and goethite were identified using TEM observations (Fig. 6D,E).

(3) Goethite in veins. As already mentioned, clusters of iron oxide crystals were also observed in some calcite veins in limestones (Fig. 2B, Fig. 7A,B), with the distinctive needle-shape indicating that they are goethite. They are precipitates and have not been altered by later geologic events.

(4) Iron sulfide (and oxide) inclusions within calcite and dolomite. Abundant opaque inclusions can be observed within crystals of both dolomite and calcite with an optical microscope. EDS analyses using the SEM revealed that most inclusions (Fig. 8) are titanium oxide, iron sulfide, and clay minerals whereas a few grains are iron oxide, as discussed below.

Magnetite (or inferred to be magnetite). Apart from the spherules observed in magnetic extracts, Ti-free magnetite is shown or inferred to be present in the following modes.

(1) Iron oxides, inferred to be magnetite, on the boundaries between residual dolomite and dedolomite. In limestone samples from the Minturn area, complete dolomite rhombs were rarely found.
but relict dolomite rhomb edges were observed in several thin sections. These dolomite rhomb edges are surrounded by a calcite matrix (Fig. 9A,B), indicating that dissolution of dolomite and precipitation of calcite had occurred. Fine-grained iron oxides were observed along the boundaries between residual dolomite rhomb edges and replacement calcite or dedolomite (Fig. 9C,D). Some iron oxides apparently precipitated in fractures between the residual dolomite and dedolomite (Fig. 9D). EDS analyses showed that iron is the only cation present in the oxides. Unfortunately, we have been unable to obtain SAED data as all attempts at ion milling have resulted in loss of the material through differential thinning of closely spaced phases.

(2) Iron oxides, inferred to be magnetite, within bitumen veins in limestones. In the older part of the Minturn section, many rock samples contain significant residual hydrocarbon or bitumen (Fig. 10A). It appears opaque when observed with an optical microscope and dark in BSE images, occurring in both veins and pore spaces (Fig. 2B, Fig. 10A). SEM observations reveal that fine-grained iron oxides are common within the bitumen veins (Fig. 10B,C). The grain sizes are generally less than 1 μm. EDS analyses indicate that iron is the only cation. For these grains as well, we have been unable to obtain SAED patterns to characterize the structure, as bitumen veins are too vulnerable to the ion milling, causing the iron oxides to be milled away along with the bitumen before the surrounding calcite walls are sufficiently thinned.
(3) Iron oxide (magnetite) within calcite and dolomite. Abundant opaque inclusions can be observed within crystals of both dolomite and calcite. EDS analyses using the SEM revealed that most inclusions are titanium oxide, iron sulfide, and clay minerals whereas a few grains are iron oxide (Fig. 8A,C). These iron oxides have irregular crystal shapes and grain sizes <1 μm. SAED patterns obtained using the STEM revealed that these fine-grained iron oxides in our dolomite samples are composed of multicrystalline magnetite (Fig. 8D,E). However, we have been unable to prepare limestone samples for STEM observations because calcite is more vulnerable than dolomite in ion milling; moreover, most of these grains are in voids within calcite crystals (Fig. 8C). The similarities in occurrence of fine-grained iron oxides in both limestone and dolomite samples suggest that the iron oxide inclusions in calcite crystals are likely the same as the magnetite inclusions in dolomite crystals. We can also conclude, importantly, that most of these grains in the voids of calcite and dolomite crystals (Fig. 8A,C) are indicative of a fluid-mediated authigenic origin.

5.3. Rock magnetic measurements

5.3.1. IRM acquisition

Isothermal remanent magnetization (IRM) acquisition curves were obtained in fields up to 1.4 T (Fig. 11). For all the studied samples, IRM was acquired rapidly up to 0.2 T and saturated near 0.3 T, indicating that low- to medium-coercivity magnetic minerals are dominant. There are no indications of significant goethite or hematite contributions to the IRM. The saturation IRM of the limestone samples is much higher than that of the dolomite samples, suggesting that precipitation of authigenic magnetite (e.g., at the boundaries between dolomite rhomb edges and dedolomite) enhanced the magnetic content of the limestones.

5.3.2. Thermal demagnetization of 3D-IRM

In order to identify ferromagnetic minerals, thermal demagnetization of 3-dimensional (3D) isothermal remanent magnetizations imparted with different coercivity windows was carried out for representative specimens that were also used in the IRM acquisition experiment. Using this method, ferromagnetic minerals with contrasting coercivities and unblocking temperatures can be distinguished (Lowrie, 1990). Our results show that the dominant magnetic minerals in all the studied specimens have low to medium magnetic coercivities (Fig. 12), consistent with results of IRM acquisition. The proportion of highest coercivity magnetizations in the z-direction from 3D-IRM thermal demagnetization results is occasionally somewhat higher than that expected from the IRM acquisition results (Fig. 11). This is likely caused by minor sample misalignment (non-orthogonality) during IRM acquisition and measurement of the remanence.

For limestone samples, all three magnetization components (x, y, and z) decay steadily with increasing temperature, with a slight hint of more rapid loss at about 370°C (Fig. 12A). There is little or no indication of major components carried by goethite or hematite, which would show up as pronounced decay of higher-coercivity components below about 120°C and above 600°C, respectively. The 3D-IRM demagnetization of limestone samples indicates that magnetite and, possibly, pyrrhotite carry the remanence.

For the dolomite samples, all three magnetization components decrease sharply below 375°C and then decay further up to 580°C. One of the dolomite samples has a high-coercivity component that remains up to 650°C (Fig. 12D), indicating that in this sample hematite can carry a very minor component of the remanence. Other dolomite samples have no hematite component (Fig. 12C), consistent with our electron microscopic observations that hematite grains are unevenly distributed throughout the dolomite samples. 3D thermal demagnetization results indicate that
Fig. 9. Electron microscope images of fine-grained oxides (magnetite?) precipitated on the boundary between residual dolomite and dedolomite. (A) and (B) BSE images of dolomite rhombs. (C) BSE images showing fine-grained iron oxides (arrows) on the boundary between residual dolomite (dark) and dedolomite. (D) BSE image showing fine-grained iron oxides (arrows) in the crack between residual dolomite and dedolomite. \( \text{Dol} = \) dolomite; \( \text{Cc} = \) calcite.
goethite does not appear to contribute to the remanence in the dolomites, even though it was detected by TEM. Unblocking temperatures for the low-coercivity (x) IRM component and NRM range up to 580°C, indicating that magnetite is likely a carrier of NRM. The substantial decrease of low- as well as higher-coercivity components at temperatures ranging up to 375°C indicates that pyrrhotite is also a major carrier of the NRM in the dolomites. Whereas the thermal demagnetization of 3D-IRM indicates the existence of hematite in some of the dolomite samples, the unblocking temperatures of the NRM
5.3.3. Low-temperature measurements of NRM and IRM

In the limestone samples, the presence of pyrrhotite is indicated by SEM/STEM observations, but whether this pyrrhotite actually carries some of the remanence is not clear. To test this, low-temperature IRM was imparted to limestone samples, which were allowed to warm up, but the transition at 34 K (Dekkers et al., 1989) characteristic of pyrrhotite was not observed, nor was there any sign of a Verwey transition characteristic of magnetite (Fig. 13). The IRM intensities decayed rapidly as the temperature increased, suggesting the presence of superparamagnetic (SP) grains; Michael Jackson has suggested (pers. commun., 1998) that especially the sharp drop below 50 K resembles the behavior of superparamagnetic particles with grain sizes around 0.010 μm. The NRM intensities were too low to be measured in low-temperature experiments.

5.3.4. Hysteresis properties

Hysteresis properties were measured for small (5–50 mg) individual limestone and dolomite specimens. The traditional parameters used in rock magnetism have been plotted in Fig. 14A, which shows that most ferromagnetic materials in these samples are in the pseudo-single domain (PSD) range (Day et al., 1977). $H_{cr}/H_c$ ratios of dolomite samples have a narrow range from 2 to 6 whereas the values for the limestone samples have a much wider range from 3 to 11 (Fig. 14A). When comparing similar $M_{rs}/M_s$ ratios, the dolomite samples have higher coercivities ($H_c$) than the limestone samples (Fig. 14B). The
values plotted in the diagram of Fig. 14A fall, not surprisingly, along the power-law trend for remagnetized carbonates published by Channell and McCabe (1994).

The hysteresis curves are clearly wasp-waisted, which may indicate that magnetic carriers with contrasting coercivity distributions co-exist in the samples; the difference ($\Delta M$) curves derived from the hysteresis plots (Tauxe et al., 1996) show some peaks and troughs of $\Delta M$ versus $H$, but of only minor importance. The wasp-waistedness can also be attributed to combinations of SP and remanence carrying (SD, PSD or MD) grains, with the presence of SP grains being supported by the low-temperature experiments (Fig. 13). We conclude that the wasp-waisted hysteresis curves are indicative of SP in addition to SD±PSD±MD grains, as well as magnetic carriers with contrasting coercivities, e.g., combinations of magnetite and hematite or possibly pyrrhotite.

5.3.5. pARM measurements

A total of four samples from limestones and dolomites were subjected to pARM experiments. Two representative results are shown in Fig. 15. The limestone samples collected from the Minturn area have lower peak values of 7.5 mT (Fig. 15A), whereas the dolomite samples collected from the Tennessee Pass area have peak values around 27.5 mT (Fig. 15B), in agreement with the results from the hysteresis experiments. According to Jackson et al. (1988), the pARM peak value is directly correlated with magnetite grain size in the sample. The measured peak values for limestone and dolomite samples correspond to average magnetite grain sizes of 5–25 $\mu$m and 2–3 $\mu$m, respectively, assuming that the major magnetic mineral in these samples is magnetite (Jackson et al., 1988). The lack of a clear bimodal distribution in the pARM experiments reinforces the hypothesis that the wasp-waistedness of the hysteresis curves is due to a contribution by SP grains and not only due to grains with different coercivities.

5.3.6. Lowrie–Fuller test

The modified Lowrie–Fuller (LF) test gives different results for limestones and dolomites. For limestones, IRM is more stable than ARM in AF demagnetization (Fig. 16A) and yields a multidomain (MD) test result (Lowrie and Fuller, 1971; Johnson et al., 1975). In contrast, ARM is more stable than IRM in AF demagnetization (Fig. 16B) and yields a single-domain (SD) or PSD test result for dolomite samples, again in qualitative agreement with the coercivities indicated by the pARM and hysteresis results.

The upward-convex shape of IRM demagnetization curves for the dolomite samples also suggests a SD or PSD behavior (Dunlop, 1983), in agreement with the LF test result, and with the relatively small (2–3 $\mu$m) diameters estimated from the pARM results. For the limestone samples, there is hardly any upward convexity in the IRM demagnetization curves. The pARM measurements suggest that the limestones are dominated by MD magnetic minerals, but the presence of SP grains is also suggested by the low-temperature experiments, indicating a broad spectrum of grain sizes.

6. Discussion

6.1. Ages of the remagnetizations

The Lower Carboniferous limestone and dolomite of the Leadville Formation in central Colorado were
Fig. 14. Plots of hysteresis parameters. (A) Plot of $M_{rs}/M_s$ vs. $H_{cr}/H_c$ (Day et al., 1977). (B) Plot of $M_{rs}/M_s$ vs. $H_c$. 
earlier studied by Horton et al. (1984) and Horton and Geissman (1990). We confirm here their interpretation that the dolomite samples from Tennessee Pass carry a late Paleozoic, likely Permian, magnetization of mostly reversed polarity (our C component), and that the limestone samples from the Minturn area contain a Late Cretaceous–early Tertiary magnetization (our A' component). Our results are different in that we have also observed a B component in limestone samples from the Minturn area and an A'' component.
in the dolomite samples from the Tennessee Pass area. The A' and A'' components are similar and have been combined (A component). Our paleomagnetic data for the Leadville Formation thus reveal three ancient magnetizations: A, B, and C.

The apparently syn-folding A component exists both in limestone and dolomite samples and has a pole position (Fig. 17) near the Late Cretaceous to early Tertiary part of the North American apparent polar wander path (APWP), as consistent with a re-magnetization during Laramide deformation (Horton et al., 1984; Fruit et al., 1995). This component was
also found in the overlying Belden Formation, called component 2 by Banerjee et al. (1997), and shown to be syn-folding as well.

Pole C shifts only slightly upon tilt correction and matches the Permian–Early Triassic APWP segment (Fig. 17). If one were to assume that the Sawatch uplift belongs tectonically to the Colorado Plateau, which has yet to be demonstrated, then a counter-clockwise correction of about 5° for the rotation of the plateau causes a slight shift in this paleopole to the direct vicinity of the Early Permian–Late Carboniferous references poles (Van der Voo, 1990). The C magnetization is interpreted, therefore, as a Kiaman-age remagnetization related to a late Paleozoic event, such as dolomitization (see Horton and Geissman, 1990).
Judging from the paleopole location of the B component, it appears to be of Late Jurassic age (Fig. 17). An alternative possibility for the B component of our study is that it is a composite magnetization, in which case thermal demagnetization in the 400–580°C interval may have caused simultaneous removal of a late Paleozoic C component and a Late Cretaceous–early Tertiary A magnetization. The pole of component B fits only with the APWP for Middle–Late Jurassic time before tilt correction or with partial tilt correction (up to about 30%). After full (100%) tilt correction, the paleopole is shifted well off the APWP (Fig. 17), suggesting that pole B is not a pre-folding magnetization. The B directions fall on a great circle between the A and C directions, permitting an interpretation of B as the simultaneous removal of A and C during thermal demagnetization (see also Fig. 3A). In AF demagnetization (Fig. 3B), the B component is not isolated (see also Horton et al., 1984). However, this magnetization resembles some component 3 directions (e.g., in the South Park area near Weston Pass, see Fig. 1) of Banerjee et al. (1997), which has been interpreted by them as being of Early Jurassic age. These component 3 directions do not fall on the great circle between the A and C directions, and — assuming that our B component and their component 3 are the same — this argues against the idea that the B component is composite. We favor the interpretation that the B component is a discrete magnetization of Late Jurassic age in the Minturn sites.

6.2. Magnetic carriers of the secondary magnetizations and their origins

Several potentially magnetic minerals have been observed with SEM/STEM and their mode of occurrence and likelihood of carrying a remanence are summarized in Table 5. Being magnetic is a necessary but not a sufficient condition for a mineral to be an NRM carrier. Rock magnetic data can provide an essential link between NRM properties and magnetic minerals observed by electron microscopy. The NRM unblocking temperature is one of the most characteristic features contributing to identification of a magnetic carrier. Based on thermal demagnetization characteristics, the samples examined contain three groups of magnetizations: a low temperature (<150°C) recent magnetization, an intermediate unblocking temperature (200–350°C) magnetization (A for both limestone and dolomite samples), and a high unblocking temperature (400–580°C) magnetization (B for limestones from the Minturn area and C for dolomites from the Tennessee Pass area).

Previously, magnetite spherules had been considered as the carrier of most of the NRM in dolomites of the Leadville Formation (Horton et al., 1984; Horton and Geissman, 1990). The spherules have also been observed in magnetic separates of Leadville limestone (Xu et al., 1994). However, detailed rock magnetic and electron microscopic observations indicate that these magnetite spherules are mostly in the multi-domain size range, with coercivities <10 mT (Xu et al., 1994). Hysteresis and pARM of the limestones reveal similar coercivities, confirming the contributions by the spherules to bulk rock magnetic properties, but these low coercivities are not compatible with AF demagnetization of the ancient NRM. Instead, it seems likely that the spherules carry only the present-day field component revealed below 10 mT in AF demagnetization.

In addition to magnetite, potentially magnetic minerals observed by SEM/STEM are hematite, goethite and pyrrhotite. Paleomagnetic and rock magnetic observations indicate that goethite and hematite do not contribute significantly to the NRM. In contrast, pyrrhotite seems clearly indicated by thermal demagnetization of NRM and 3D-IRM as a remanence carrier in the dolomites. Pyrrhotite normally has a maximum unblocking temperature of 325°C (Lowrie, 1990), but higher maximum unblocking temperatures (up to 350°C) were found in fine-grained pyrrhotite by Rochette et al. (1990). The 3D-IRM thermal demagnetization results from dolomite samples show that pyrrhotite is a major magnetic mineral in the dolomites (Fig. 12C,D). We argue that the A' magnetization of the dolomite samples from the Leadville Formation is likely carried by pyrrhotite and that it is, therefore, a chemical and not a thermoviscous remanence. In the limestones, pyrrhotite is observed by SEM/STEM, but it is not clear whether it carries the A' remanence. However, the identical unblocking temperatures of the A' and A'' magnetizations with the same Cretaceous–Tertiary age and the high (>70 mT) coercivities in AF demagnetization (Fig. 3B) suggest that these
magnetizations are likely carried by the same magnetic carrier, i.e., pyrrhotite, although the pyrrhotite component is not as obvious in the 3D-IRM thermal demagnetization results of limestone samples as it was for dolomite samples.

Four types of magnetite were observed, or inferred to be present, in the limestones and dolomites (Table 5), in addition to the spherules already discussed above. Some or all of these types of oxides (magnetite, or inferred to be magnetite) are likely to be the carriers of the B and C magnetizations, because of their maximum unblocking temperatures of 580°C, consistent with the Curie temperature \( T_C \) of magnetite. Certainly we can exclude goethite and pyrrhotite as the carriers of the B and C magnetizations, because these minerals have much lower \( T_C \)s, whereas hematite is unlikely because of its typically much higher coercivities in addition to unblocking temperatures that generally persist up to 680°C, the Néel temperature of hematite.

The Leadville Formation in the studied area has never been buried to a depth greater than 5000 m (De Voto, 1990). Nuccio et al. (1989) determined that the local geothermal gradient within the central Colorado rift basins has been as high as 40° to 48°C/km and that this likely occurred during Ancestral Rocky Mountain deformation in the Late Carboniferous and Early Permian. The estimated maximum paleotemperatures in the studied area then would have been \(~240°C\), which is significantly less than temperatures required to activate a viscous partial thermoremanent remagnetization in magnetite that would resemble the C magnetization. This is true regardless of whether the model of Pullaiaiah et al. (1975) or that of Middleton and Schmidt (1982) is used for theoretical relaxation time-unblocking temperature relations, indicating that the B and C magnetizations are likely chemical remanent magnetizations carried by authigenic magnetite. This conclusion was also reached by Banerjee et al. (1997) for their component 3. Inside the mineralized zone, where we did not sample, hydrothermal temperatures have likely been higher, e.g., up to 380°C, as estimated from fluid-inclusion homogenization temperatures (Beaty et al., 1990).

The four (non-spheroidal) types of magnetite or magnetite (?) observed by electron microscopy are (see Table 5): (1) low-Ti magnetite that has grown authigenically on secondary minerals such as quartz, chlorite or albite; (2) magnetite (?) grown at the boundaries between relict dolomite rhomb edges and dedolomite; (3) magnetite (?) in bitumen veins; and (4) magnetite as inclusions in dolomite and magnetite (?) as inclusions in calcite.

Of these four types, the limestones and dolomites have only type (4) in common, whereas types (1), (2) and (3) are found exclusively in the limestones. Type (4) magnetite, therefore, seems to be the likely carrier of the C magnetization in the dolomites. The observation that limestones have a higher NRM intensity than the dolomites, is consistent with a different magnetic carrier that has enhanced the NRM in the limestones but not in the dolomites. Type (1) magnetite must generally have \( T_C \)s less than 500°C, because of its Ti and Mn content (Table 6); therefore, this type of magnetite cannot be the only carrier of the B magnetization with its unblocking temperatures up to 550°C (Fig. 3A, Fig. 12A). It is also less likely that type (3) magnetite is the principal carrier of the B magnetization, because bitumen was present in only some of our samples. Thus, it appears by process of elimination that type (2) magnetite is the most likely carrier of the B magnetization. If this is true, the inferred Jurassic age of the B magnetization can be linked to the timing of the formation of magnetite grains at the boundaries between dolomite and dedolomite. This, in turn, would suggest that the dedolomitization process occurred during the Jurassic.

Lastly, we turn to the interesting observation that some authigenic magnetite contains minor Ti and Mn. Solid solution of titanium in magnetite is normally associated with primary magnetite of high-temperature metamorphic or igneous origin. In MORB, for instance, titanomagnetite commonly has ulvospinel contents of \(~60\%\). Our observations of type (1) magnetite, with ulvospinel contents of up to 15%, and growing on quartz, albite, and chlorite, is seemingly incompatible with a low-temperature origin. Because the quartz, albite, and chlorite are authigenic, the euhedral magnetite growing on them must also be authigenic and formed during diagenesis. However, it is well known that metastable phases, formed during the process of low- to medium-temperature diagenesis, tend to have chemical compositions that are not compatible with the chemical com-
position extrapolated from high-temperature phase diagrams (e.g., Li et al., 1994), i.e., they did not form in equilibrium conditions. Small amounts of Ti in some of the type (1) magnetite, therefore, are not inconsistent with a diagenetic origin of the magnetite. However, to our knowledge, such authigenic low-Ti magnetite has not been described in the literature before, although earlier we have observed euhedral, authigenic magnetite with low Ti content in the Jurassic Twin Creek Limestone of western Wyoming (Xu et al., 1992).

7. Conclusions

Our electron microscope observations form a crucial link between the rock magnetic parameters that define the characteristics of the magnetic carriers, and the paleomagnetic measurements in the general area (ours, as well as the directions of Horton et al., 1984, and Banerjee et al., 1997), which constrain the ages of the magnetization. While a large variety of potentially magnetic minerals has been identified, by a process of elimination we conclude that the most likely carrier of the A magnetization component is pyrrhotite in the dolomites and possibly also in the limestones, whereas the B and C magnetizations are chemical remanent magnetizations (CRMs) carried by SD–PSD magnetite of authigenic origin. These magnetizations were acquired in Jurassic and late Paleozoic times, respectively. The latter conclusion was also reached by Banerjee et al. (1997) for their component 3. They related its origin to burial diagenesis. We infer that in the limestones, dedolomitization may have contributed to the authigenesis of the magnetite that carries the B magnetization.

The A magnetization is not of thermoviscous origin as inferred by Horton et al. (1984) and Banerjee et al. (1997), which would be possible if the magnetization were carried by magnetite, but is not likely for the (pyrrhotite) carrier we have identified in the dolomites. Whereas ambient temperatures during the Late Cretaceous–early Tertiary may have contributed to the formation of the pyrrhotite, the most likely remanence in this magnetization carrier is a CRM or a thermochemical remanence (TCRM), because estimated paleo-temperatures in that time interval were not high enough, i.e., much less than the ~350°C needed for the complete thermal resetting that could cause a pure TRM in pre-existing pyrrhotite. Instead of relating the A magnetization to intrusions in the greater area (Horton et al., 1984), we prefer to explain it by relating it to the sulfide mineralizations that occurred in the area during the Tertiary (Beaty et al., 1990).

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