QUANTIFYING SHALE MINERALOGY AND ANISOTROPY FROM LOW TEMPERATURE MAGNETIC SUSCEPTIBILITY MEASUREMENTS

Vivian T. Ebufegha and David K. Potter

Department of Physics, and Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Canada

This paper was prepared for presentation at the International Symposium of the Society of Core Analysts held in Snowmass, Colorado, USA, 21-26 August, 2016

ABSTRACT

Shales can exhibit significant variations in mineral composition and anisotropy, which can affect their petrophysical and geomechanical properties. These variations are important for determining the integrity of shales as caprocks, and for optimizing hydrocarbon recovery techniques (such as hydraulic fracturing) where shales form unconventional reservoirs. We describe a novel technique to rapidly and non-destructively quantify the mineralogy and anisotropy of shale samples from low temperature magnetic susceptibility measurements. This involves cooling the samples in liquid nitrogen, and measuring their average (bulk) magnetic susceptibility and anisotropy of magnetic susceptibility (AMS) as a function of temperature as the samples warm to room temperature. For paramagnetic minerals, such as illite clay (a key component in many shales), magnetic susceptibility decreases with increasing temperature according to the Curie law, whereas for diamagnetic minerals (such as quartz) magnetic susceptibility is independent of temperature. We show how the variation with temperature can be used to quantify the paramagnetic versus diamagnetic mineral content. We show how the paramagnetic (mainly illite) versus diamagnetic (mainly quartz) mineral content in the shale samples can be estimated from low temperature measurements by comparing the results with our theoretical temperature dependent magnetic susceptibility curves for such mineral mixtures. Experimental results from some well characterized synthetic samples also gave similar results. Anisotropy of magnetic susceptibility (AMS) was also determined by performing separate warming runs (from low temperatures to room temperature) in 9 different orientations for several samples. The increased paramagnetic signal at low temperatures significantly enhanced the magnitude of the AMS compared to standard room temperature measurements in most cases. This allowed us to identify anisotropy in some samples that was not obvious at room temperature. More significantly, changes in the AMS with temperature also enabled us to separate out contributions to the AMS from different minerals. For example, we could distinguish normal AMS fabrics dominated by paramagnetic minerals, inverse AMS fabrics due to stable single domain ferrimagnetic particles, and inverse AMS fabrics that appear to be due to iron enriched carbonates.

INTRODUCTION

Low temperature magnetic susceptibility measurements provide a potential tool for quantifying paramagnetic versus diamagnetic mineral components in shales, and for identifying anisotropy in weakly anisotropic samples conventionally measured at room temperature. A key advantage of low temperature measurements is that the paramagnetic signal is significantly larger than that at room temperature and above. Another advantage is that low temperature measurements are unlikely to induce chemical changes, whereas heating significantly above room temperature may do (unless the sample is vacuum sealed). The present study details a series of low temperature magnetic susceptibility measurements undertaken on Horn River shale samples (from British Columbia) from a 200 m cored section that penetrated all of the Muskwa, Otter Park and Evie formations. We show how the measurements can be used to quantify the illite clay content, identify anisotropy, and how changes in the orientations of the principal anisotropy axes can be related to the mineral components in the samples.

SAMPLES AND METHODS

Sample Preparation

54 samples in total were prepared from the following Horn River formations: 10 from the Muskwa, 18 from the Upper Otterpark, 20 from the Lower Otterpark and 6 from the Evie. Due to the friable nature of some shale samples, and to ensure minimal alteration of the original rock fabric prior to taking directional magnetic susceptibility measurements, the samples were impregnated with sodium silicate (Na_2SiO_3) adhesive prior to cutting following the method described by Ebufegha and Potter [1]. Sodium silicate is weakly diamagnetic so has negligible effect on the magnetic susceptibility and anisotropy of magnetic susceptibility results. The samples were impregnated with the sodium silicate by soaking for three to five minutes and left to dry overnight before cutting into 2.2 cm × 2.2 cm × 2.2 cm cubes under a jet of propylene glycol.

Low Temperature Magnetic Susceptibility Curves

Magnetic susceptibility measurements of the shale samples were taken between ~173 K (-100 °C) and room temperature 294 K (21 °C). Each sodium silicate impregnated sample was first cooled to approximately 173 K by immersion in liquid nitrogen for 45 minutes. Since magnetic susceptibility and temperature could not be measured simultaneously, the temperature as a function of time as the sample warmed up from 173 K to room temperature was first measured using a thermocouple placed in a small hole drilled on the surface of the sample. The sample was then cooled a second time by immersion in liquid nitrogen for 45 minutes. Following this second cooling, the magnetic susceptibility with time was measured using a Bartington MS2B meter as the sample warmed up to room temperature. This static meter is unidirectional, measuring susceptibility in one direction for each application of a low field of 80 A/m to a sample of known mass in a 10 cm^3 sensor cavity. The instrument measures the magnetization induced in the sample by the applied magnetic field and calculates the ratio between the induced magnetization and the applied field (the magnetic susceptibility). The graphs of temperature as a function of time and magnetic susceptibility as a function of time can be combined to get the magnetic susceptibility as a function of temperature.

Mineral quantification using low temperature magnetic susceptibility curves: theoretical and experimental curves for illite + quartz mixtures

To quantitatively determine mineral concentrations, theoretical curves of magnetic susceptibility with temperature for illite (paramagnetic) + quartz (diamagnetic) mixtures were compared to the experimental curves for the Horn River shale samples. The theoretical curves were determined for such mixtures because XRD results from Makhanov [2] showed that they are the primary paramagnetic and diamagnetic minerals in the Horn River Group. As a general protocol we recommend some initial XRD, if possible, so that the appropriate mineral mixtures are modelled by the low temperature magnetic measurements. Whilst calcite is the main diamagnetic mineral in the Evie formation, calcite would have given very similar results since quartz and calcite have quite similar magnetic susceptibilities. For paramagnetic minerals the magnetic susceptibility depends on temperature according to the Curie Law as follows (whereas for diamagnetic minerals the magnetic susceptibility is independent of temperature):

$$M/B = C/T \qquad (1)$$

where M is the magnetization, B is the applied field, M/B is the magnetic susceptibility, C is a mineral specific Curie constant, and T is the absolute temperature in Kelvin. At a given temperature, the magnetic susceptibility is the sum of the contributions of all of its mineral components. For a sample consisting of illite and quartz, magnetic susceptibility per unit mass χ_T is given by the expression from Potter [3]:

$$\chi_T = \{(F_I)\ (\chi_I)\} + \{(1 - F_I)\ (\chi_Q)\} \qquad (2)$$

where F_I is the fraction of illite, $(1 - F_I)$ is the fraction of quartz, and χ_I and χ_Q are the room temperature mass magnetic susceptibilities of illite and quartz ($15 \times 10^{-8}\ m^3\ kg^{-1}$ and $-0.55 \times 10^{-8}\ m^3\ kg^{-1}$ respectively). Using equation (1), χ_T is then used to calculate the mixture's Curie constant C, which is in turn used to calculate χ_T for progressively lower temperatures. Theoretical susceptibility-temperature curves were determined for 11 mixtures of illite and quartz. We also tested some synthetic quartz + illite mixtures.

Low Temperature Anisotropy of Magnetic Susceptibility (AMS) Profiles

At progressively lower temperatures, the orientations and magnitudes of the principal AMS axes increasingly reflect the concentrations and petrofabric of paramagnetic minerals present in a sample. To determine the AMS with temperature at least 9 directional susceptibility measurements are required. Therefore nine curves of magnetic susceptibility with temperature were determined for each sample using the same procedure as in the "Low Temperature Magnetic Susceptibility Curves" section above. For each measurement temperature, the AMS was determined and percent AMS was calculated as follows:

$$100(\chi_1 - \chi_2) / \chi_3 \qquad (3)$$

where χ_1, χ_2 and χ_3 are the max, int and min magnetic susceptibilities. This was undertaken for 18 of the 54 sodium silicate impregnated Horn River Group samples.

RESULTS AND DISCUSSION

Low Temperature Magnetic Susceptibility Curves and Mineral Quantification

Figure 1 shows how magnetic susceptibility varies with temperature in the various Horn River shale formations. There is an inverse relationship between magnetic susceptibility and temperature as described by the Curie law. The progressive increase in magnetic susceptibility with decreasing temperature is due to the presence of paramagnetic minerals (since diamagnetic susceptibility is independent of temperature, and the susceptibility of the ferrimagnetic mineral magnetite above the Verwey transition, 120 K, is also approximately constant with temperature). The theoretical magnetic susceptibility curves with temperature for the 11 mixtures of quartz and illite are shown in **Figure 2**, along with some of the experimental results from **Figure 1.** The curves are labelled with the percent illite and quartz. The curves were used as templates for determining the illite content in the shale samples (shown in **Figures 3** and **4**) and could equally be used to determine the quartz content. Note that we tested some experimental curves for synthetic illite + quartz mixtures (not shown for clarity), which also gave very similar results.

As an independent check of the illite content we compared the magnetic susceptibility results with some geochemical data from inductively coupled plasma mass spectrometry (ICP-MS). The general formula for illite is $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$ and its aluminium oxide concentration varies from 25% to 45% [4]. Since most of the aluminium oxide (Al_2O_3) in shales is found in clays, Al_2O_3 concentration was used to verify the magnetic susceptibility derived clay concentrations. **Figure 3** shows a crossplot of percent Al_2O_3 and percent illite from our measurements, and **Figure 4** shows a comparison of the two parameters with depth. The Al_2O_3 data was not available at every depth where we made low temperature susceptibility measurements, so only illite contents at depths close to those for which Al_2O_3 data were available are compared in **Figures 3** and **4**. A good correlation between the percent illite derived from the low temperature magnetic susceptibility curves and the percent aluminium oxide suggests that the illite content determined from low temperature magnetic susceptibility measurements in meaningful. For most samples we determined the illite content from the temperature dependent magnetic susceptibility in just one orientation (black open symbols), the x-axis. For some samples we determined the illite content from an average value from 9 orientations in the sample (i.e., we took account of the anisotropy of these samples). These are the red solid symbols in **Figures 3** and **4,** and they show an even better correlation with the Al_2O_3 data in **Figure 3** (with the regression coefficient $R^2 = 0.85$).

Low Temperature Anisotropy of Magnetic Susceptibility (AMS)

Figure 5 compares AMS at 294 K (room temperature) and AMS at 200 K for the 18 samples measured. The AMS is enhanced for most samples at low temperature. This is due to the increased paramagnetic signal. **Figure 6** shows the progressive change in percent AMS with decreasing temperature for two individual samples. The difference between room temperature AMS and AMS at a lower temperature is due solely to the paramagnetic phases in a sample. Note that the sample in the lower figure shows very weak AMS at room temperature (and would be regarded as virtually “isotropic” by conventional room temperature AMS measurements), but exhibits a significant AMS at 200 K. **Figure 7** shows the change in the directions of the maximum and minimum AMS axes as a function of temperature from low temperature (around 200 K) to room temperature (294 K). The figure shows representatives of the 4 main cases that were observed. **Figure 7 (a)** shows a sample with a normal sedimentary AMS fabric that remains normal at low temperature (maximum susceptibility close to horizontal and minimum susceptibility close to vertical). The different points represent different temperatures (the temperature values are not shown for clarity). The results for this sample indicated a signal dominated by paramagnetic illite clay (85% illite as determined from our theoretical template curves). In contrast **Figure 7 (b)** shows a sample with an inverse AMS fabric that remains inverse at low temperature (maximum susceptibility close to vertical and minimum susceptibility close to horizontal). This suggests a decreased illite content (64% as determined from our theoretical template curves) and the additional presence of a strongly paramagnetic mineral that can cause an inverse fabric. Ihmlé et al. [5] and Schmidt et al. [6] have documented such fabrics due to the presence of paramagnetic ferroan calcite or siderite whose c-axis is its maximum susceptibility axis [7]. Carbonates are seen in thin sections of this shale sample.

Figure 7 (c) shows a sample that has an inverse AMS fabric at low temperature but progressively changes to a normal AMS fabric at room temperature. This can happen if there is a mixture of a paramagnetic clay (such as illite), some ferrimagnetic material (particularly if it is multidomain) and a strongly paramagnetic iron bearing carbonate (such as siderite). Depending on the contents of each mineral the low temperature signal may be dominated by the more strongly paramagnetic iron bearing carbonate, giving rise to an inverse AMS fabric (as in **Figure 7 (b)**). As the sample warms up the paramagnetic clay and ferrimagnetic material may dominate the magnetic susceptibility signal at room temperature giving rise to the normal AMS fabric. **Figure 7 (d)** shows a sample that has a normal AMS fabric at low temperature but changes to an inverse AMS fabric at room temperature. This can arise if the sample contains a mixture of a paramagnetic clay (such as illite) and some uniaxial stable single domain (SSD) ferrimagnetic material (such as fine grained magnetite). At low temperature the signal may be dominated by the enhanced magnetic susceptibility of the paramagnetic clay, giving rise to the normal AMS fabric. As the sample warms up the paramagnetic clay signal decreases and the ferrimagnetic signal starts to dominate. A uniaxial SSD grains has a maximum magnetic susceptibility perpendicular to its long (easy) axis [8], which gives rise to the inverse AMS fabric. Subsequent anisotropy of magnetic remanence (AMR) measurements were consistent with the presence of uniaxial SSD particles in this sample.

CONCLUSIONS

1. Low temperature magnetic susceptibility measurements have been demonstrated to provide a relatively quick and non-destructive method of quantifying paramagnetic mineral content (in this case illite clay) in shale samples, by comparing experimental temperature dependent magnetic susceptibility results with theoretical curves. The

percentage illite content correlated well with independent geochemical data (the percentage Al_2O_3), providing evidence that the magnetic results were meaningful.

2. The variation in the orientation of the principal anisotropy of magnetic susceptibility (AMS) axes between room temperature and low temperature gives important information regarding the mineral components in the samples:

- Samples with normal AMS fabric orientations that didn't change significantly with temperature contained predominantly paramagnetic clay (illite), whereas the paramagnetic signal from samples with inverse AMS fabrics that didn't change with temperature were dominated by iron bearing carbonates.
- Samples with a normal AMS fabric at room temperature and an inverse AMS fabric at low temperature contain a mixture of clay, small amounts of ferrimagnetic material, and iron bearing carbonate. The clay/ferrimagnetics dominated at room temperature and the iron carbonate dominated the signal at low temperature.
- For samples with an inverse AMS fabric at room temperature and a normal AMS fabric at low temperature, the room temperature signal was dominated by the presence of uniaxial stable single domain ferrimagnetic particles, whereas at low temperature the enhanced paramagnetic signal of the illite clay dominated.

3. The enhanced AMS at low temperature enables one to identify anisotropy in samples that appear to be "isotropic" from conventional room temperature measurements.

ACKNOWLEDGEMENTS

The support of an NSERC Discovery Grant to DKP is gratefully acknowledged.

REFERENCES

1. Ebufegha, V. T. and Potter, D. K., 2014. A comparison of quantitative techniques for determining the 3D anisotropy of shale samples: application to Horn River Basin shales, British Columbia, Canada. In *Proceedings of the 2014 International Symposium of the Society of Core Analysts, 8-11 September 2014,* Avignon, France. Paper SCA2014-011 (12 pages).
2. Makhanov, K. K. 2013. An experimental study of spontaneous imbibition in Horn River shales. M.Sc. thesis, University of Alberta, Edmonton, Canada, pp. 109.
3. Potter, D. K., 2007. Magnetic susceptibility as a rapid, non-destructive technique for improved petrophysical parameter prediction. *Petrophysics,* **48**, (issue 3), 191-201.
4. Manning, D. A. C., 1995. Introduction to industrial minerals. Springer, pp. 288.
5. Ihmle, P.F., Hirt, A. M., Lowrie, W. and Dietrich, D., 1989. Inverse magnetic fabric in deformed limestones of the Morcles Nappe, Switzerland, *Geophysical Research Letters*, **16**, 1383–1386.
6. Schmidt, V., Hirt, A. M., Hametner, K., Günther, D. 2007. Magnetic anisotropy of carbonate minerals at room temperature and 77 K. *American Mineralogist*, **92**, 1673–1684.
7. Jacobs, I. S., 1963. Metamagnetism of siderite. *J. Applied Physics,* **34**, 1106-1107.
8. Potter, D. K. and Stephenson, A., 1988. Single-domain particles in rocks and magnetic fabric analysis. *Geophysical Research Letters*, **15**, 1097-1100.

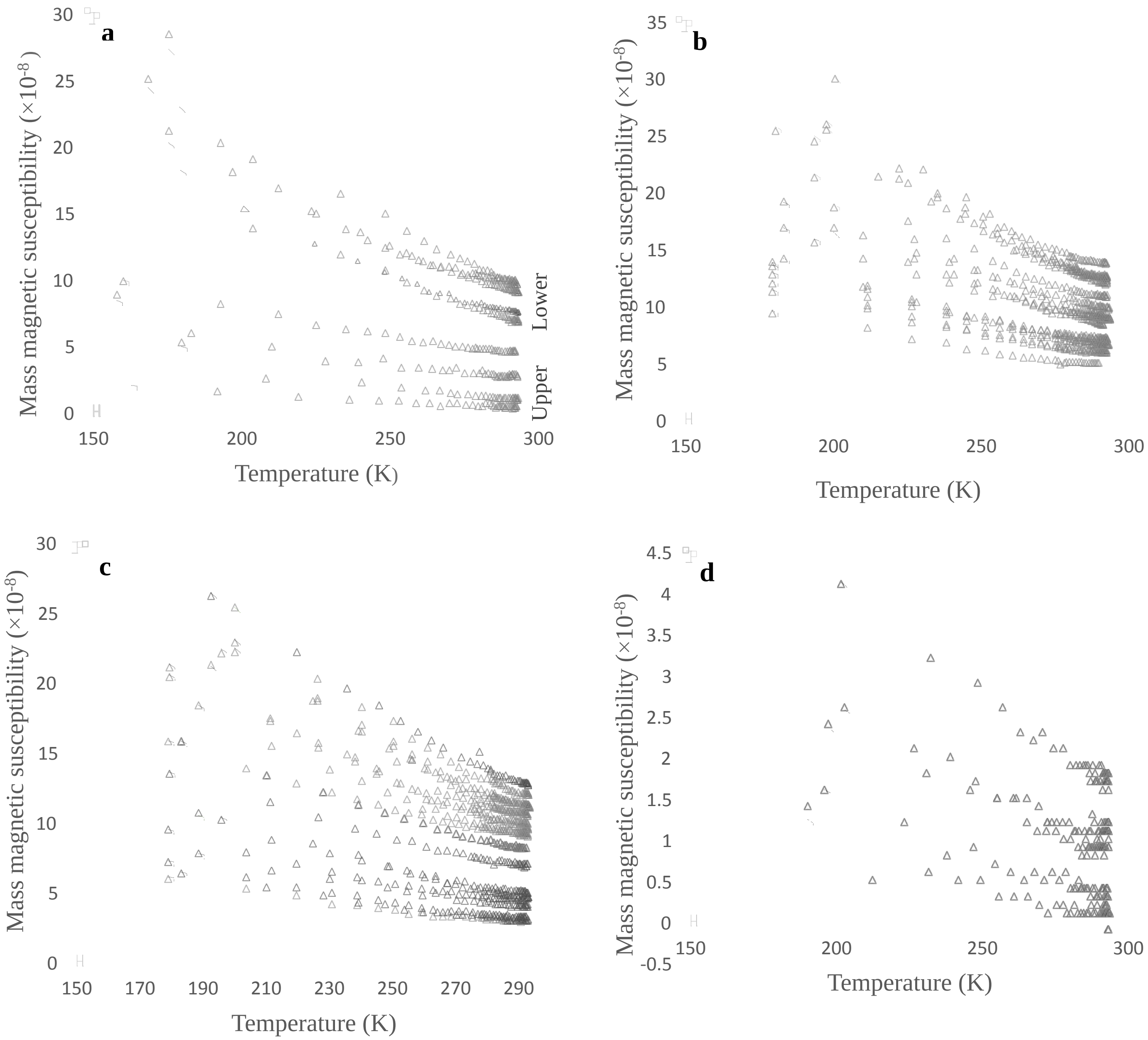


Figure 1. Low temperature magnetic susceptibility curves for shale samples in the following formations of the Horn River Group, British Columbia, Canada (a) Muskwa, (b) Upper Otter Park, (c) Lower Otter Park and (d) Evie formations. The units for the mass magnetic susceptibility axes are m^3 kg^{-1}.

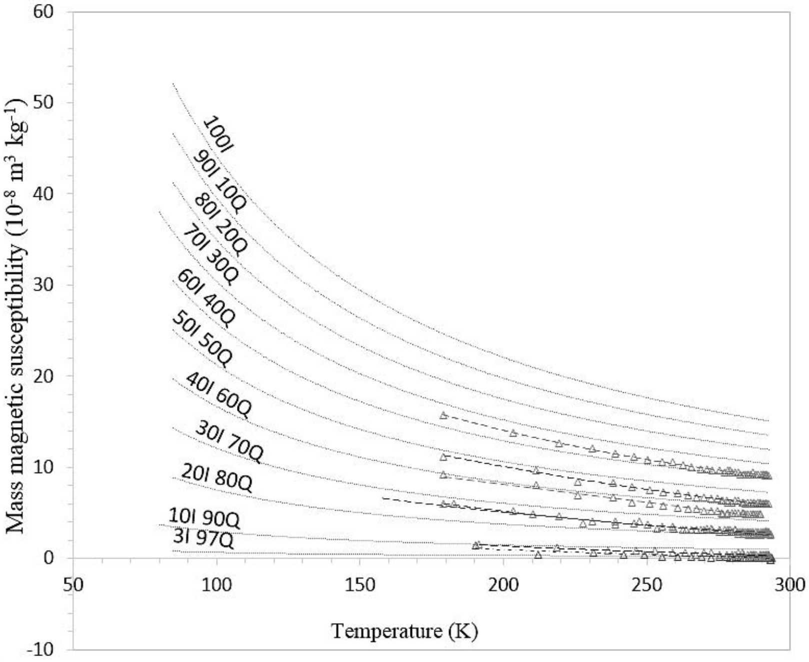


Figure 2. Theoretical mass magnetic susceptibility curves with temperature, along with some experimental results. Labels indicate the illite and quartz percentages (e.g., 90I 10Q is 90% illite and 10% quartz).

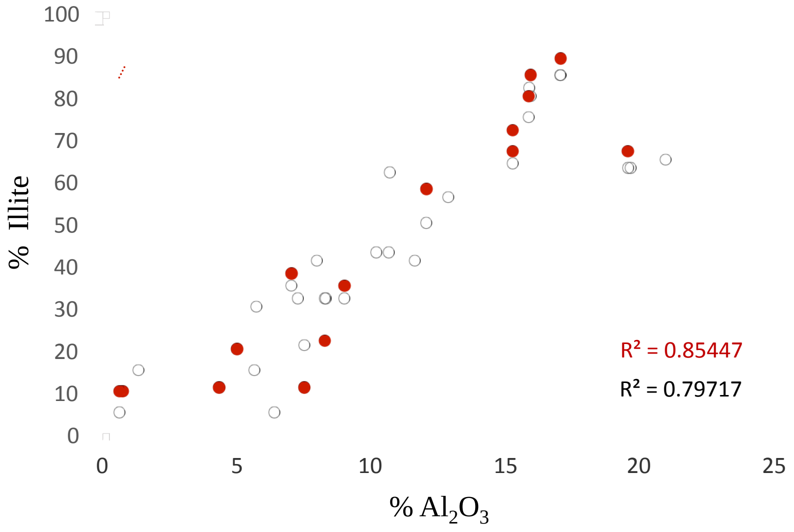


Figure 3. Crossplot of percent Al_2O_3 from geochemical data against percent illite content determined from the template curves of **Figure 2**. The solid red points represent an average illite content determined from 9 magnetic susceptibility orientations in the sample, whereas the open black symbols represent the illite content determined from just 1 orientation in the sample (along the x-axis).

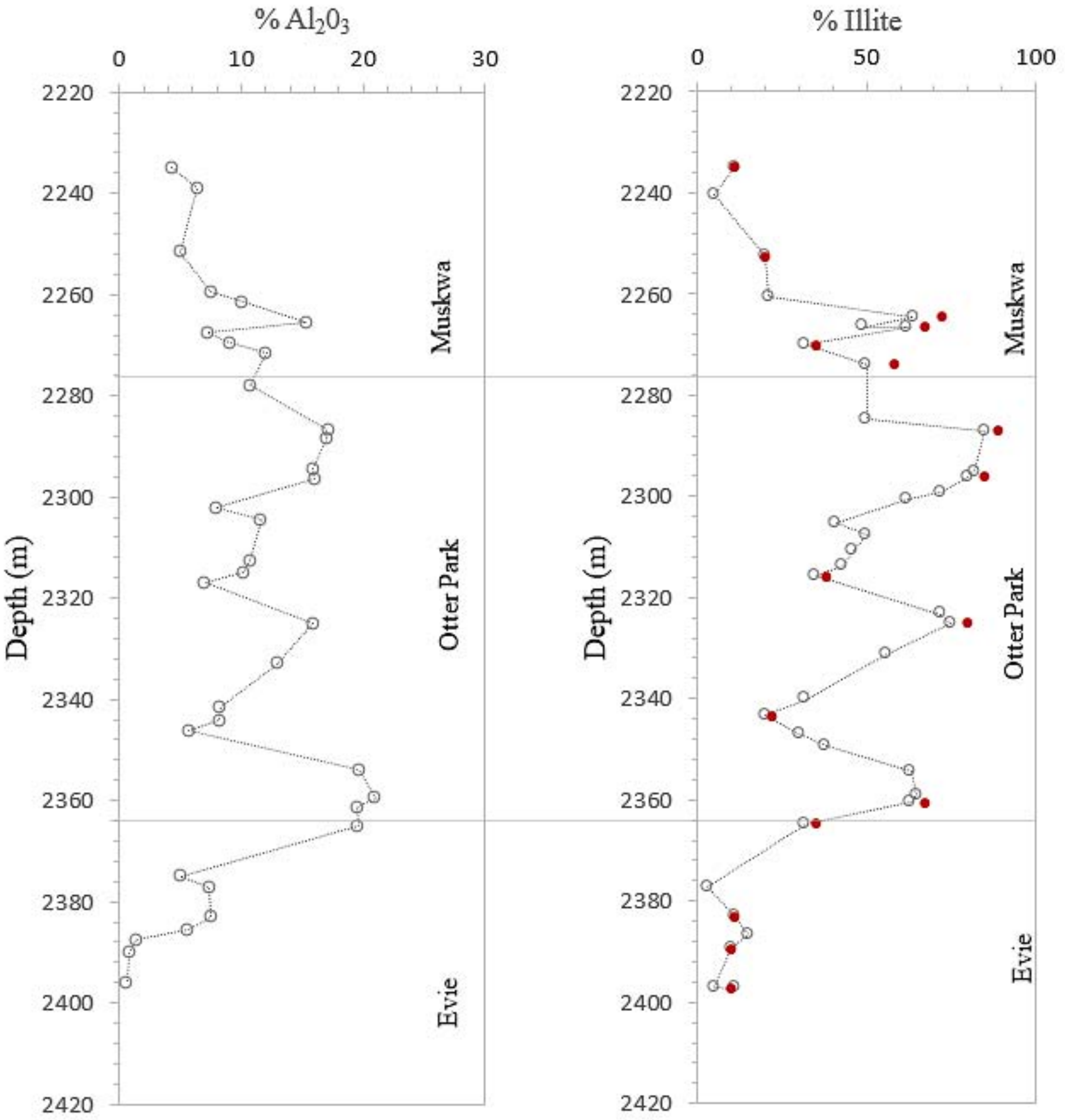


Figure 4. Percent illite derived from the low temperature magnetic susceptibility curves and percent Al_2O_3 composition from geochemical data with depth in the Horn River Group. The solid red points for the illite profile represent an average illite content determined from 9 magnetic susceptibility orientations in the sample (i.e., the anisotropic nature of the samples is accounted for), whereas the open black symbols represent the illite content determined from just 1 orientation in the sample (along the x-axis).

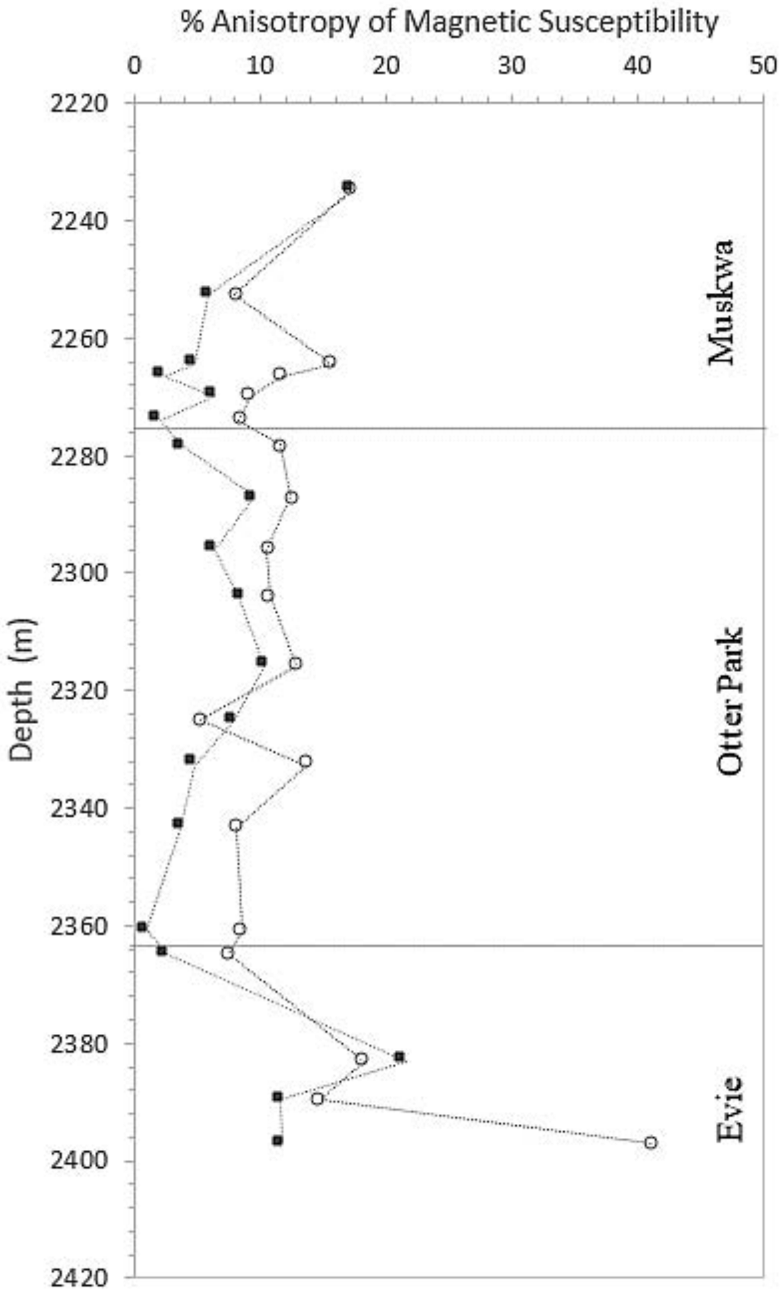
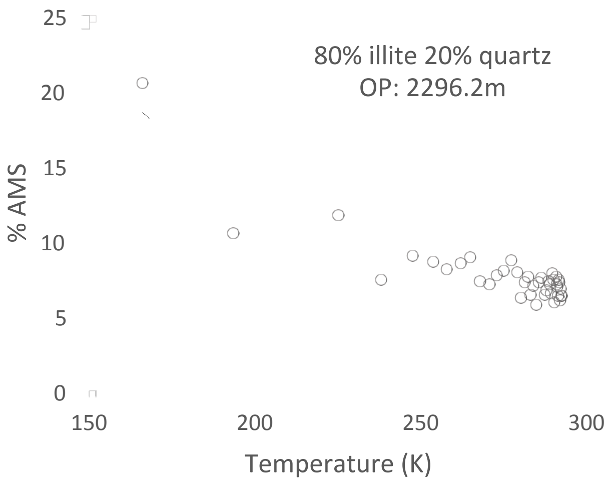


Figure 5. Comparison of anisotropy of magnetic susceptibility (AMS) with depth in the Horn River Group at room temperature 294 K (solid symbols) and AMS at 200 K (open symbols).



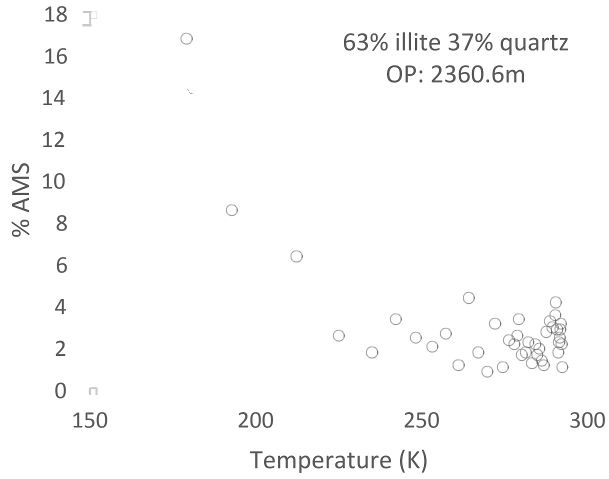


Figure 6. Variation of percent AMS with temperature for two Horn River Group samples from the Otter Park formation with different illite contents. Note that the sample in the lower figure shows very weak anisotropy at room temperature, but exhibits significantly higher AMS at lower temperatures.

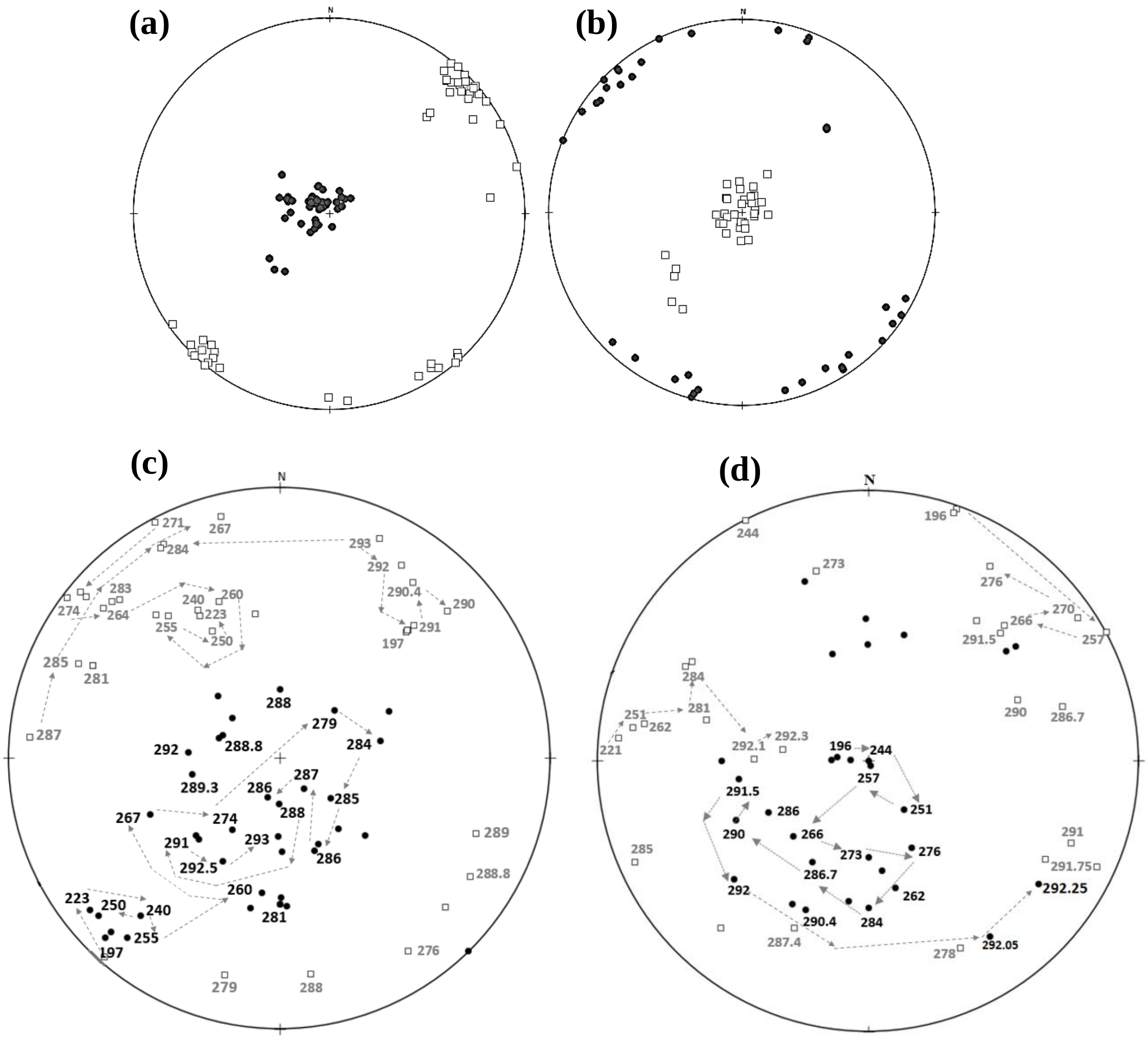


Figure 7. Stereographic projections showing variation in AMS type (in terms of the orientation of the principal AMS axes) with temperature for the Horn River Group samples: (a) Sample with a normal AMS fabric irrespective of temperature. Maximum magnetic susceptibility (open squares) is close to horizontal (parallel to the bedding plane) and minimum magnetic susceptibility (solid circles) is close to vertical (normal to the bedding plane). (b) Sample with an inverse AMS fabric irrespective of temperature. Maximum magnetic susceptibility (open squares) is close to vertical and minimum magnetic susceptibility (solid circles) is close to horizontal. (c) Sample where the AMS is normal at room temperature and becomes inverse with decreasing temperature. Numbers represent the temperature in degrees Kelvin. (d) Sample where the AMS is inverse at room temperature and becomes normal with decreasing temperature. Numbers represent the temperature in degrees Kelvin.