Major-element geochemistry of pelites

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INTRODUCTION

Metapelites are metamorphosed clay-rich sedimentary rocks (e.g., shales and mudstones). They are widespread in the rock record, and ever since the pioneering work of George Barrow (1893), they have been useful as indicators of metamorphic grade because their mineral assemblages are sensitive to changing pressure and temperature (P-T) conditions (Hietanen, 1967; Pattison and Tracy, 1991; Spear, 1993). Several compilations of the geochemical compositions of metapelites have been assembled and their values compared to those of unmetamorphosed shales (Shaw, 1956; Ague, 1991). Although average pelite compositions are rarely the same, making strict comparisons difficult. Thus, there remains uncertainty over what truly is an average pelite, and how much compositional variability pelites show.

A related topic of debate is the degree to which elements are redistributed during the devolatilization that accompanies prograde metamorphism (Ague, 1991; Stepanov, 2021). While mass transfer of major elements can be significant in domains of high fluid flux (e.g., veins, skarns, and sometimes along lithologic contacts), mass transfer away from these domains is thought to be broadly negligible (Ague, 2011, 2017). Despite this, small variations in several of the most important major elements (e.g., Al, K, Mg, Fe++, and Fe++) can lead to different mineral compositions, proportions, and, in turn, assemblages (Spear, 1993). Therefore, it is important to assess the degree of major-element mobility during prograde metamorphism, since this underpins our assumption that a single bulk composition can be used for phase diagram calculations across a range of metamorphic grades.

We present a new compilation of published pelitic whole-rock analyses ranging in metamorphic grade from shales to granulite-facies gneisses. It is ~20 times larger than any previous compilation. We used this database to document the range in chemical compositions of pelites, provide an average pelite composition, and assess whether there are any significant compositional changes as a function of metamorphic grade.

NEW COMPILATION OF LITERATURE

Several previous studies compiled bulk compositional data from the literature in order to assess major-element compositions of pelites and possible changes with metamorphic grade (Lapadu-Hargues, 1945; Shaw, 1956; Ague, 1991). Since these studies, the number of published pelitic whole-rock analyses in the literature has increased considerably, and many unpublished theses containing analyses are now available online. Using these, we constructed a new database of 5729 analyses from 364 studies categorized into 103 regions. Only individual rock samples that had been crushed and analyzed using bulk techniques such as wet chemistry or X-ray fluorescence (XRF) were included. Samples from domains of high fluid flux (e.g., described as selvedge or coming from vein margins) were excluded from the database because they have been subject to localized mass transfer. The following major rock-forming components were analyzed in all samples: SiO₂, TiO₂, Al₂O₃, FeO, MnO, MgO, CaO, Na₂O, and K₂O. Where reported by the authors of the previous studies, we also included determinations of P₂O₅, Fe₂O₃, and loss-on-ignition (LOI). For wet chemical analyses, we combined H₂O, CO₂, and SO₂ together as an estimate for LOI (e.g., volatile content), as was done by Ague (1991). The Supplemental
Material describes in detail the methodology used to exclude nonpelitic analyses; categorize the samples according to metamorphic grade; and portray the data in Al2O3-FeO-MgO (AFM) diagrams involving compositional projection. A complete catalog listing all analyses, including the sample name, metamorphic zone, literature reference, and whole-rock data in weight percent, is available in the Supplemental Material.

Due to the large number of analyses in the database, we were able to divide the samples into finer-scale metamorphic grade–related categories than previous studies (cf. Shaw, 1956; Ague, 1991) while maintaining >250 analyses in each category (Fig. 1). Nine zones were defined: diagenetic, anchizone, chlorite, biotite, garnet, porphyroblast, subsolidus sillimanite or K-feldspar, migmaticite, and garnet-cordierite (Grt-Crd). Other mineral abbreviations are after Warr (2021).

| Figure 1. (A) Pressure-temperature distribution of metapelitic zones used in this study: diagenetic (Diag), anchizone (Anch), chlorite (Chl), biotite (Bt), garnet (Grt), porphyroblast (Porph), subsolidus sillimanite or K-feldspar (Sil-Kfs), migmaticite (Migm), and garnet-cordierite (Grt-Crd). Other mineral abbreviations are after Warr (2021). (B) Histogram of the number of analyses in each zone. |

TREATMENT OF DATA PROJECTIONS

Projection of bulk compositions into an AFM diagram (Fig. 2A; Thompson, 1957) permits visualization of the variation in the three main compositional variables of pelites, namely, Al, Fe, and Mg. It also allows the compositional effects of varying modal proportions of quartz and plagioclase feldspar in the original sedimentary protolith to be filtered out. Whole-rock analyses comprising 9–12 components (see above) were reduced to the six-component KFMASH (K2O-Fe2O3-MgO-Al2O3-SiO2-H2O) system using projections from apatite, ilmenite, albite, and anorthite to remove P2O5, TiO2, Na2O, and CaO, respectively. All iron was assumed to be FeO (ferrous), and MnO was omitted. To plot the KFMASH analyses in an AFM diagram, further projection from quartz (SiO2), hydrous fluid (H2O), and either muscovite or K-feldspar (K2O) was required. Given that the majority of samples in the database were muscovite-bearing samples, the AFM diagram in Figure 2A shows all samples projected from muscovite (A1M). Figure S2 includes diagrams projected from K-feldspar, as well as diagrams separating lower-grade, muscovite-bearing samples from higher-grade, K-feldspar–bearing samples.

Statistical Analysis

Geoscientists commonly use the mean and standard deviation to describe the compositional variation in major-element geochemical data sets. However, of the various methods used to assess “average” values, the mean and standard deviation consistently perform the worst because they are the most susceptible to outliers (Rook, 1988; Woronow and Love, 1990). Therefore, we used the median and the interquartile range as the most representative measures of the average and the spread of the whole database, as well as subsets of data. When assessing possible grade-related variations, the mean is additionally shown for comparison (Fig. 3). Compositional data are inherently multivariate, have a constant sum, and in turn are constrained by the closure problem (Rollinson and Pease, 2021). To ensure that correlations observed in our grade-related assessment did not result from the interdependence of weight percent oxide values (Chayes, 1960), we transformed compositional data using log10 compositional mass ratios (Aitchison, 1982). Drawbacks of this approach are that a choice must be made for the conserved element in the ratios, and that log ratios are sometimes difficult to interpret. We found that trends between log ratio and weight percent oxide graphs were similar (Fig. S3), and thus we only show weight percent oxide values in Figure 3.

COMPOSITIONAL VARIABILITY

AFM Diagrams

Of the 5729 analyses, 409 plotted at anomalously low or high A1M values (>1.0 or <−0.4; A1M = molar [Al2O3/(3 × K2O)]/[Al2O3 – (3 × K2O) + FeO(ferro)+ + MgO]), and those are not shown in Figure 2A. Most analyses plotted between XFeO = 0.30–0.55 [XFeO = projected molar MgO/(MgO + FeO(ferro))] and A1M = 0.0–0.4, with our median worldwide pelite plotting at XFeO = 0.42 and A1M = 0.19 (Fig. 2A; Table 1). There was a strong clustering midway between the AFM plotting positions of garnet and chlorite in the AFM diagram and no clear distinction between high- and low-Al pelites (cf. Spear, 1993, his figure 10-3; see Fig. 2A herein).

Ferric Iron

There were 1964 analyses in the database for which FeO was measured using titration, permitting an estimate of the whole-rock ferric/ferric iron ratio. Figure 2B shows that most analyses plotted between XFe3+ = 0.30–0.55 [XFe3+ = molar MgO/(MgO + FeO)] and XFe3+ = 0.1−0.3 [XFe3+ = 2 × Fe2O3/(2 × Fe2O3 + FeO)], with
the highest density at $X^*_{Mg} \sim 0.4$ and $X_{Fe^{3+}} \sim 0.2$. The median worldwide pelite has $X_{Fe^{3+}}$ of 0.23 and $X^*_{Mg}$ of 0.46 based on these 1964 samples, compared to $X^*_{Mg}$ of 0.39 [$X_{Mg} = \text{molar } \text{MgO}/(\text{FeO}^{\text{tot}} + \text{MgO})$] for all 5729 samples assuming all iron is FeO (Table 1).

Regional Analysis

In order to determine if it is justified to use the above median pelite composition to compare $P$-$T$ conditions in different metamorphic belts, we calculated median compositions for 11 regions and/or orogens in the database for which there were more than 100 analyses. Most of these regional median values clustered together, with compositions similar to the worldwide median pelite (Fig. 2; Table 1). Exceptions included the Moine (Scotland) and Sanbagawa (Japan) regions, which had lower $A^{Mg}$ values, the Buller (New Zealand) region, which had higher $X^*_{Mg}$, and the Alpine (Austria, Italy, and Switzerland) region, which had higher $X_{Fe^{3+}}$.

Metamorphic Grade

Previous authors have reported a decrease in both volatile content and $X_{Fe^{3+}}$ with increasing metamorphic grade (Shaw, 1956; Ague, 1991). We found a consistent decrease in LOI across all metamorphic grade (Shaw, 1956; Ague, 1991). While pelitic compositions occur over a range of AFM values, there is a strong clustering of analyses at $X^*_{Mg} \sim 0.4$ and $A^{Mg} \sim 0.2$, with no separation between high- and low-Al pelites (Fig. 2A). AFM for most regions cluster together (Fig. 2; Table 1), implying that it is justified to compare the inferred $P$-$T$ conditions of commonly occurring metapelitic mineral assemblages between different orogens. An unexpected result of our study is the relatively high median whole-rock $X_{Fe^{3+}}$ of 0.23, given that $X_{Fe^{3+}}$ in oxides and silicates in metapelites other than hematite, magnetite, and muscovite are lower than this value, and muscovite has low absolute Fe$^{3+}$ (Forshaw and Pattison, 2021). This question requires further study.

Previous studies differ concerning whether there is significant bulk compositional change in major elements as a function of metamorphic grade: Some authors have argued for progressive change in bulk composition with increasing grade (Lapadu-Hargues, 1945; Ague, 1991, 1997), while others have argued that metamorphism is essentially isochronal apart from the loss of volatiles and reduction of iron (Shaw, 1956; Vidale, 1974; Atherton and Brotherton, 1982; Walther et al., 1995; Moss et al., 1996; Stepanov, 2021). While we found a continuous decrease in volatile content across the full range of metamorphic grades, median $X_{Fe^{3+}}$ only decreased markedly from the diagenetic to biotite zones and remained relatively constant at higher grades (Fig. 3). After accounting for these differences by normalizing analyses to 100% on a volatile-free basis with all iron converted to FeO, there were still distinct differences in concentrations of elements for certain metamorphic zones. Examples include lower median SiO$_2$ and higher median Al$_2$O$_3$ and $A^{Mg}$ for the porphyroblast and subolus sillimanite or K-feldspar zones, and higher median MnO in the garnet zone.

Ague (2011, 2017) demonstrated that mass transfer is an important process in domains of high fluid flux and more minor away from these domains. While our database excluded samples...
Described as or interpreted to have been affected by metasomatism, the low SiO₂ values in the porphyroblast and subsolidus sillimanite or K-feldspar zones could result in part from the increase in silica solubility with metamorphic grade (Manning, 1994). Alternatively, differences may be explained by sampling bias, in which especially aluminous layers containing abundant, petrologically significant porphyroblasts may have been preferentially sampled by petrologists in the field (e.g., Walther et al., 1995; Stepanov, 2021). The preferential sampling by metamorphic petrologists is perhaps best exemplified by the following quote: “In collecting and sectioning pelitic rocks, minimum variance specimens were emphasized, so that samples were biased in favor of rocks containing several of the phases staurolite, garnet, sillimanite, andalusite, and cordierite” (Holdaway et al., 1982, p. 574).

Despite the above considerations, the size of our database and the fact that it incorporated a wide range of metamorphic grades and geographic locations mean that analyses were not skewed toward a single metamorphic zone. Therefore, phase diagram modeling using the median worldwide pelite presented in this paper (Table 1) should allow broad comparison of the P-T conditions of different pelitic mineral assemblages and of different metamorphic terrains.

**ACKNOWLEDGMENTS**

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**REFERENCES CITED**


**TABLE 1. MEDIAN PELITE COMPOSITIONS**

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<thead>
<tr>
<th>Region or Orogen</th>
<th>n</th>
<th>SiO₂</th>
<th>TiO₂</th>
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<th>Fe₂O₃</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
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<td>4.11</td>
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<td>0.42</td>
<td>0.21</td>
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<tr>
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<td>0.79</td>
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<td>0.48</td>
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*Note: All iron is shown as FeO* proj with volatiles (loss-on-ignition [LOI], H₂O, CO₂, and SO₂) removed and values renormalized to 100%. X₉₅, X₅₀, X₀₅, A₉₅, A₅₀, and A₀₅ are defined in the text; n—number of analyses. Number in parentheses is the number of analyses with measured FeO and Fe₂O₃. See the Supplemental Material (see text footnote 1) for locations of each region.*