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Q4 2 Characterization and acid-mobilization study for typical iron-bearing clay mineral

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ABSTRACT

In this study, iron speciation in five standard clay samples, which are generally observed in 20 Q8
mineral dusts, was characterized. Iron mobilization from these clays was then measured in 21
acidic media. For comparison, a commercially available Arizona test dust (ATD) was also 22
observed. The results showed that the free-Fe contents of clays were commonly lower than 23
that of dust aerosols. The components of clays were dominant by the structural Fe held in 24
the aluminosilicate lattice but with distinct mineralogical signatures. After 36 hr, total iron 25
solubility of the clays measured in the 0.1 N H₂SO₄ solution ranged between 3.3% and 5.9%, 26
and followed in the order of KGa-2 > SWy-2 > CCa-2 > IMt-2 > NAu-2. The Fe solubility of 27
clays was not positively correlated with total Fe content or the specific surface area. Based 28
upon the Mössbauer spectrum and transmission electron microscopy (TEM) analysis, the Fe 29
(II) fraction and the Fe/Si ratio of clay particles changed after dissolution, suggesting the 30
total Fe solubility depended on the Fe atom states existing within the aluminosilicate 31
lattice. The Fe in KGa-2 and SWy-2 was most likely substituted for alkaline elements as the 32
interlayer ions held by ionic bonds in the aluminosilicate, which are more liable to 33
dissolution. However, the Fe in NAu-2 was more likely to be bound by strong covalent bonds 34
in aluminosilicate mineral, which is less soluble. The much highly soluble Fe (12.6%) in ATD 35
was not only linked to the dissolution of an appreciable fraction of Fe(II), but also could be 36
attributed to the fact that the Fe bonds in the clay fraction of ATD were mainly present as 37 Q9
ionic bonds. The TEM images showed that reacted clay particles displayed less aggregate 38
particles, with nanoparticle aggregates and the Fe/S-rich tiny particles attached to the 39
remains. 40

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54 **Introduction**

55 Fe is an essential element for the synthesis of protochlorophyllide, especially in the high nutrient low chlorophyll
 56 (HNLC) regions (Martin, 1990; de Baar and Boyd, 2000; Chen
 57 et al., 2017). Aerosol deposition provides a major input of the
 58 bioavailable iron to the open ocean, therefore affects the
 59 global biogeochemical cycles and the climate system (Baker
 60 and Jickells, 2006; Duce and Tindale, 1991; Jickells et al., 2005;
 61 Mahowald et al., 2009). The flux of atmospheric bioavailable
 62 Fe to the surface ocean is controlled by the deposition flux and
 63 the Fe solubility (Martin, 1990; Boyd et al., 2010; Raiswell and
 64 Canfield, 2012). Mineral aerosol source of iron is estimated to
 65 represent approximately 95% of the global atmospheric iron
 66 budget, and the volcanic and anthropogenic sources only
 67 account for the remaining 5% (Mahowald et al., 2005). Mineral
 68 dusts prior to uplift are produced by physical and chemical
 69 weathering in the source regions of primary and then
 70 transported in the atmosphere over a long time. These
 71 processes shape the properties of the dust precursors and
 72 therefore determine the nature and amount of Fe in the dust,
 73 as well as soluble fraction of Fe (Shi et al., 2011a; Baker and
 74 Croot, 2010). Mineral dust is a complex entity typically
 75 containing a mixture of several Fe-bearing minerals including:
 76 ferrihydrite and other poorly crystalline Fe phases, crystalline
 77 hematite, goethite, magnetite, and Fe-bearing clay minerals
 78 such as illite, kaolinite, and smectite (Shi et al., 2009; Arimoto
 79 et al., 2002; Lafon et al., 2004; Formenti et al., 2008; Lázaro
 80 et al., 2008; Avila et al., 1997; Shi et al., 2012).

81 It was well documented that a long range transport would
 82 result in a decrease of quartz relative to the clay fraction
 83 because of the more rapid removal of quartz, which has the
 84 relatively larger mass median diameter of quartz (Mahowald
 85 et al., 2005). Dust deposition modeling showed that the clay
 86 fraction becomes more and more dominant on the downwind
 87 of the sources from Asia (Gao et al., 2001). In the African dust
 88 collected over Atlantic Ocean and Mediterranean, the clay
 89 group represented between 48% and 82% of the total aerosol
 90 mass, illite and kaolinite were the dominant minerals,
 91 smectite and chlorite were detected but in low concentrations
 92 (Journet et al., 2008). The relative abundances of the clay
 93 minerals, such as illite and kaolinite, have been used to trace
 94 the regional origins of Saharan dust over the North Atlantic
 95 Ocean and northeastern Spain (Avila et al., 1997; Caquineau
 96 et al., 1998). It was concluded that illite is a major clay species
 97 in the mineral dust aerosols originating from Sahara and the
 98 Asian continent (Chester et al., 1977; Glaccum and Prospero,
 99 1980; Merrill et al., 1994). Kaolinite is the major one hosted by
 100 the dust originating from Sahel (Lafon et al., 2004; Chester
 101 et al., 1972). Chlorite, illite and kaolinite are major clay species
 102 in Chinese soils (Biscaye et al., 1997). Chad basin soils are
 103 essentially clayey, with a majority of kaolinite, illite and
 104 smectite (Herrmann et al., 1999). Kuskulana glacial flour
 105 contains a significant fraction (26%) of Fe-bearing smectite, a
 106 typical weathering product of volcanic ash deposits (Prudencio
 107 et al., 2002). Total iron contents of clay minerals are often up to
 108 25 wt% (Hofstetter et al., 2003), which is much higher than an
 109 average iron concentration of 3.5% in crustal materials (Duce
 110 and Tindale, 1991). But the Fe content of clay minerals can be

highly variable. Even in the same type of clay, the Fe contents
 111 differ greatly. For example, the illite standard sample IMt-1
 112 collected from Montana contained 66% more Fe than the illite
 113 standard sample API35 from Fithian Illinois (Shi et al., 2012;
 114 Journet et al., 2008; Paris et al., 2011). The chemical heterogene-
 115 ity is due to the parent/primary mineral from which the clay
 116 minerals originated, and/or the chemical weathering regimes in
 117 soils (Meunier and Velde, 2004). 118 119

The solubility of Fe varies greatly among the desert dusts
 120 from the different regions, and the associated Fe speciation is
 121 an important factor (Baker and Croot, 2010; Aguilar-Islas et al.,
 122 2010). Both Fe oxides and clay minerals in atmospheric dust
 123 are formed during chemical weathering of parent minerals
 124 and are in intimate physical association with each other (Shi
 125 et al., 2011b). As soil develops, more and more of the primary
 126 and secondary Fe-bearing minerals decompose and the Fe of
 127 their lattice structure is converted to Fe oxides (Shi et al.,
 128 2012). By examining the iron release from a few mineral
 129 components, including feldspars, clays and iron oxides, it was
 130 found that the most bioavailable fraction of iron in dust is not
 131 the iron oxides (e.g., hematite), but the clay component, which
 132 accounts for more than 90% of the soluble iron (Shi et al., 2009;
 133 Journet et al., 2008). Because the Fe in the clay fraction of the
 134 dust are mainly present as ionic bonds or amorphous
 135 impurities, which are more liable to dissolution (Journet
 136 et al., 2008), previous researches have confirmed that iron-
 137 bearing clays play a particularly important role in providing
 138 bioavailable Fe to HNLC waters (Journet et al., 2008; Schroth
 139 et al., 2009), and argued that it is the clay minerals alone that
 140 control the apparent Fe solubility in the dust (Shi et al., 2009,
 141 2012; Journet et al., 2008). 142

Two significant phases of iron have been suggested, namely,
 143 “free-iron” in the form of oxide or hydroxide discrete particles,
 144 and “structural iron”, which are trapped in the crystal lattice of
 145 aluminosilicate minerals (Lafon et al., 2004). Free-iron in
 146 atmospheric mineral aerosols occur mainly either as hematite
 147 or goethite (Claquin et al., 1999), and sometimes ferrihydrite
 148 (nominally $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$), but to a much low degree (Shi et al.,
 149 2009). On the basis of Journet’s work, structural iron could be
 150 divided into two forms: i) Fe is located in the octahedral (Al-
 151 bearing) or tetrahedral (Si-bearing) layers bound by covalent
 152 bonds in the case of nontronite and beidellite, and ii) Fe is
 153 substituted by Mg and K, and held by ionic bonds in the lattice,
 154 such as in the minerals of orthoclase, illite and montmorillon-
 155 ite. It was proposed previously that the solubility is much higher
 156 for the amorphous Fe as compared to the Fe in oxides or bound
 157 by covalent bonds in the aluminosilicate matrix (Journet et al.,
 158 2008). The solubility of the Fe which substitutes Si and Al in the
 159 lattice is lower than that replaces alkaline elements as
 160 interlayer ions (Journet et al., 2008). Although iron solubility
 161 could be heavily influenced by iron speciation in clay minerals,
 162 there is lack of direct laboratory measurement on iron
 163 mobilization from clays. 164

The aim of this study was to understand deeply how the
 165 nature of Fe minerals in the clay affects its Fe solubility, hence
 166 affecting the Fe biogeochemical cycle. Five ubiquitous types of
 167 standard iron-bearing clay mineral, including nontronite,
 168 chlorite, illite, kaolinite and smectite, were employed to explore
 169 the linkage between iron speciation in the clay minerals and
 170 properties of iron solubility. The clay minerals were analyzed 171

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